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INTRODUCTION TO
PAPER ELECTROPHORESIS
AND RELATED METHODS
by
MICHAEL LEDERER
Institut du Radium, Paris

To the biochemist, the medical chemist, the organic scientist and all chemical research workers this book brings the fundamental principles and techniques employed in the rapidly developing field of paper electrophoresis, which can now be considered as a general method of analysis. This companion volume to E. and M. Lederer's earlier work on Chromatography includes —

- the theory of paper electrophoresis
- numerous applications to biochemistry and to organic and inorganic chemistry
- outlines of further possibilities of the use of this technique
- methods for micro-analytical studies
- a basis for original research in the technique as it relates to particular problems

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Col. = Colorimetric, heterometric, photometric and spectrophotometric analysis(*) — colorimétrie, hétérométrie, photométrie et spectrophotométrie* — heterometrische, kolorimetrische, photometrische and spektrophotometrische Analyse*
El. = Electrical methods (except polarography) — Méthodes électriques (excepté polarographie) — Elektrische Methoden (ausgenommen Polarographie)
Grav. = Gravimetric and thermogravimetric (**) analysis — Gravimétrie et thermogravimétrie (**) — gravimetrische und thermogravimetrische (**) Analyse
Id. = Identification reactions and qualitative analysis — indentification (réactions) et analyse qualitative — Identifizierungsreaktionen und qualitative Analyse
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THE APPLICATION OF STERIC HINDRANCE TO THE SYNTHESIS OF SELECTIVE REAGENTS FROM THE 2,4,6-TRINITROPHENOLS

by

CARL E. MOORE*, MARY M. LALLY, ROBERT L. ANDERSON, JOHN L. BRADY AND JOHN J. McLAFFERTY

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Of the various recognized factors affecting selectivity, only a few offer possibilities of controlled modification. Among these is the electron distribution in the reagent molecule, a factor which has been the subject of numerous researches reported in the current and older literature[1,2]. The basicity of bonding groups, which is directly related to electron densities, usually has been altered either by ortho or para substitution in aromatic ring systems or by alpha substitution in aliphatic chains of groups of varying electronegativities.

Another method by which the basicity of functional groups can be altered is the steric hindrance of a resonating system in which the basicity of the groups under study is in part resonance controlled. Recently we have attempted to apply this approach to the synthesis of some 2,4,6-trinitrophenols with hindrance in the 3 and 3,5 positions. Picric acid, a reagent that has been the subject of many papers, was chosen as a point of departure because this type molecule appeared to offer great possibilities for modification. It is a very acidic phenol, being almost as strong an acid as the mineral acids. This great gain in acid strength over unsubstituted phenol, a very weak acid, is doubtlessly a result of several factors. These factors, which are difficult to evaluate on an individual basis, often are divided arbitrarily into various effects[3]. Among these may be listed the effects of inductance, resonance, steric hindrance, polarizability, and of the solvent. While it is difficult to separate these effects in the 2,4,6-trinitrophenols, it is accepted that the nitro groups, when unhindered, tend to lie in the plane of the ring and greatly enhance the acidity of the -OH substituent. The strong acidity is indicative of a relatively less negative region around the phenolic oxygen in picric acid in contrast to the corresponding oxygen in unsubstituted phenol. Thus is follows that the picrate anion is a much weaker base than the phenolate anion. It appears that the oxygen in the resonance-stabilized picrate anion should be much less polarized by the positive field of a cation than the oxygen in the relatively basic anion derived from a substituted (and resonance-hindered) picric acid. This variation in the polarizability of the oxygen should lead to differences in the amount of covalent character in the bond formed between the reagent and metal cation. In turn this would be expected to lead to differences in solubility, if the other influences of the substituents are small. Likewise differences in selectivity might be hoped for with varying amounts of steric hindrance.

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* Inquiries should be addressed to this author.

In testing this hypothesis several factors need to be considered in the selection of a meta-substituent for hindering purposes. These are (1) size, (2) geometry, (3) solvent interaction, and (4) electronegativity of the group. Of these, group size does not appear to be so important as the group geometry. Straight chain aliphatics, because of the tetrahedral character of the carbon atom, extend out of the plane of the ring and offer little more hindrance than a methyl group, while as expected, branching at the alpha carbon offers much greater hindrance[4]. Substituents expected to show a strong solvent interaction have not been introduced into the meta position because such substitution would introduce another set of variables which would tend to mask the properties of the reagent under study. Electronegativity effects are thought to be small in comparison to steric effects because the hindering groups are meta to the -OH, for substitution meta to a functional group in an aromatic ring system, in general, has relatively small effect on the basicity.

Table I contains the pKa's of the trinitrophenols studied.

TABLE I

pKa's OF SOME 2,4,6-TRINITROPHENOLS

Compound	*pKa*
Methylpicric acid	2.8
Ethylpicric acid	3.0
Isopropylpicric acid	3.4
Dimethylpicric acid	3.3
Methylethylpicric acid	3.3
Methylpropylpicric acid	3.6

EXPERIMENTAL PART

The compounds studied were synthesized by methods previously reported[4,5,6,7]. With exception of 3-methyl-5-*n*-propylphenol all the phenols were commercially available.

The sodium salts are conveniently prepared by dissolving the reagent in hot alcohol and making the solution alkaline with 10% NaOH. To this solution is added a saturated aqueous solution of NaCl until precipitation starts. The mixture is then chilled in an ice-salt bath and the yellow sodium salt removed by filtration and recrystallized from water. The reagents were employed as the sodium salts in concentrations varying from one to three percent. Since several of the ions under test give insoluble hydrous oxides or carbonates in alkaline media, the pH of the reagent solutions were adjusted to 5-6.

Table II contains the compounds and the cations tested.

TABLE II

Compound	NH_4^+	K^+	Mg^{+2}	Ca^{+2}	Sr^{+2}	Ba^{+2}	La^{+2}	Ce^{+2}	Pb^{+2}	Ag^+
Methylpicric acid	—	—	—	—	—	—	—	—	—	—
Ethylpicric acid	—	—	—	—	—	—	—	—	—	—
Isopropylpicric acid	—	—	—	—	—	—	∓	—	∓	—
Dimethylpicric acid	∓	∓	—	—	+	+	∓	∓	+	—
Methylethylpicric acid	∓	∓	—	—	—	+	+	+	+	—
Methylpropylpicric acid	∓	∓	—	—	—	+	—	+	+	∓

∓ 1 ml of reagent will produce a precipitate with 1 ml of 0.1*M* ion.

+ 0.2 mg of ion in 1 ml will produce a precipitate with 1 ml of reagent.

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DISCUSSION OF RESULTS

The results in Table II indicate that the highly hindered compounds display a high degree of selectivity. The methylpropylpicric and methylethylpicric acids precipitate barium quantitatively but do not precipitate strontium in $0.1M$ solutions. The dimethylpicric acid precipitates strontium and barium but not calcium. Methylpropylpicric acid likewise does not precipitate lanthanum but precipitates cerium, lead, and silver. It is interesting to note that the substituted picric acids thus far prepared begin to show selective behavior when the compounds become moderately weak acids (pKa's 3.3 and greater). This is contrary to what might be expected on the basis of a decrease of acidity alone and is probably attributable to steric effects.

ACKNOWLEDGEMENT

We are indebted to the Research Corporation for a grant in aid for this problem.

SUMMARY

Six 3 and 3,5 substituted trinitrophenols have been investigated as analytical reagents. A high degree of selectivity is shown by the highly hindered compounds.

RÉSUMÉ

Six trinitrophénols substitués en 3 et 3,5 ont été examinés pour être utilisés comme réactifs analytiques. Une grande sélectivité est observée avec les composés dont l'empêchement stérique est grand.

ZUSAMMENFASSUNG

Die Eignung von sechs 3 und 3,5-substituierten Trinitrophenolen als analytische Reagenzien wurde untersucht. Dabei hat sich herausgestellt, dass die Verbindungen mit starker sterischer Hinderung besonders selektiv reagieren.

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OXIDATIONS WITH ALKALINE PERMANGANATE USING MONOVALENT THALLIUM FOR THE BACK TITRATION

VI. ESTIMATION OF TRIVALENT ANTIMONY

by

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Antimony can be estimated by oxidizing the trivalent form to the quinquevalent state using bromate[1], iodate[2], bromine[3], dichromate[4], permanganate[5], ferricyanide[6] and ceric[7] solutions. It can also be determined by reducing the quinquevalent form by chromous and titanous[8] solutions or by precipitation as sulphide[9].

TOMICEK[10] applied alkaline permanganate for the potentiometric determination of trivalent antimony by titrating the latter in presence of telluric acid and 0.2N sodium hydroxide. The back titration of $KMnO_4$ with trivalent antimony has not yet been studied in detail nor has there been up to now a method available that depends upon oxidation of Sb^{+3} with excess permanganate followed by back titrating excess oxidant. The redox potential of the SbO_3^-/SbO_2^- system in alkaline medium amounts to —0.589 as compared with —0.670[11] for the AsO_4^{-3}/AsO_2^- couple. The equilibrium constants for the reactions leading to the reduction of permanganate to MnO_2 or manganate amount to $2\cdot10^{-120}$ or $1\cdot10^{-40}$ respectively, as compared with $1\cdot10^{-128}$ and $1\cdot10^{-42}$ for the respective reactions with arsenite[12]. These values indicate that the reactions between permanganate and these reductants take place quantitatively.

However, in the reduction of permanganate with arsenite previously studied[12] the reactions were beset with some difficulties presumably due to the strong reducing action of arsenite. Whether this is the case with antimony or not is the subject of the present investigation. It is aimed to develop a scheme for the estimation of antimony by oxidation with alkaline permanganate.

EXPERIMENTAL

The antimonous solutions were prepared from the trichloride by dissolving it either in 2.4N HCl (Sb^{+3} ions) or 0.2N sodium hydroxide (SbO_2^- ions) and from the potassium antimonyl tartrate by dissolving in distilled water containing little alkali. The antimonous content of the solutions was determined by the bromate method[1].

The permanganate solution, the titration device and the experimental technique are the same as in previous investigations[13].

RESULTS

Titration of trivalent antimony with potassium permanganate

From the results shown in Table I it is clear that on performing the titrations in the absence of telluric acid, the end-points approach the theoretical values based on the reduction of MnO_4^- to MnO_2 (although not quantitative) only at alkalinities lower than 0.4*N* NaOH and when the solutions titrated are of the order of 0.1 to 0.03*N* with respect to trivalent antimony. At alkalinities higher than this limit reduction of permanganate passes almost completely to Mn_2O_3 but the results are not good. The titration curves obtained under these conditions (Fig. 1) are each characterized by two inflections at the end-points, the first of which is sharp and corresponds to the formation of Mn_2O_3, whereas the second is smaller and less defined. More reliable results are obtained in presence of telluric acid but in this case reduction of permanganate is checked at the Mn^{+4} stage, provided that the alkali concentration is kept within certain limits which depend on the concentration of the antimony in

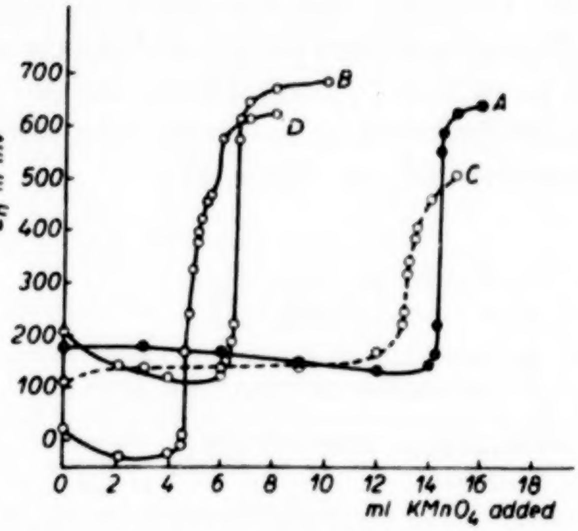

Fig. 1. (A) 5 ml 0.245*N* antimonyl tartrate in 2.5*N* NaOH × 0.1422*N* $KMnO_4$ in the presence of telluric acid;
(B) 5 ml 0.1108*N* Sb^{+3} in 1.5*N* NaOH × 0.1422*N* $KMnO_4$ in the presence of telluric acid;
(C) 10 ml 0.001108*N* Sb^{+3} in 0.5*N* NaOH × 0.001422*N* $KMnO_4$ in the presence of telluric acid;
(D) 5 ml 0.1108*N* Sb^{+3} in 1.3*N* NaOH × 0.1422*N* $KMnO_4$.

TABLE I

TITRATION OF TRIVALENT ANTIMONY WITH $KMnO_4$ IN THE ABSENCE OF TELLURIC ACID

Alkalinity	*Trivalent antimony titrated ml*	*Max. inflection per 0.1 ml $KMnO_4$ mV*	*Theoretical end-point ml*	*Exptl. end-point ml*	*Error %*
Titration of 0.1108*N* Sb^{+3} with 0.1422*N* $KMnO_4$					
0.4*N* NaOH	10	78	12.99 (MnO_2)	12.53	−3.54
1.3*N* ,,	5	156	4.87 Mn_2O_3	4.67	−4.10
1.5*N* ,,	10	68	9.74 ,,	9.55	−1.95
2*N* ,,	10	56	9.74 ,,	9.70	−0.41
2.5*N* ,,	10	190	9.74 ,,	9.74	nil
Titration of Sb^{+3} in 0.2*N* NaOH with 0.1422 $KMnO_4$					
0.1*N* NaOH	10 ml 0.0348*N*	212	4.08 (MnO_2)	3.89	−4.65
1.5*N* ,,	10 ,, ,,	162	3.06 Mn_2O_3	3.08	+0.65
2*N* ,,	25 ,, 0.032*N*	206	7.03 ,,	7.06	+0.43
2.5*N* ,,	25 ,, ,,	70	7.03 ,,	6.88	−2.13

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solution (Table II). The position of the end-point is in most cases dependent on the concentration of both alkali and reactants. Thus with the more concentrated solutions titrated (0.245 and $0.1715N$ potassium antimonyl tartrate), the alkali concentration could be varied from 1.5-$2.3N$ without any serious effect on the result (Table II).

With the antimony solutions prepared in $2.4N$ HCl less accurate results were obtained in case of the $0.1N$ solutions possibly due to partial precipitation of SbOCl which escapes oxidation. With the more dilute solutions (containing lower HCl concentrations) the errors decreased, but the best results were obtained at lower alkalinities. As is apparent from the data shown in Table III the alkalinity of the solution should be lower the lower the concentration of antimony, in order to obtain good results. Good end-points are also attained if an antimoniate solution ($\sim 0.03N$) in $0.2N$ NaOH is titrated, provided that the alkali concentration is kept between 0.25-$0.5N$ NaOH. At higher alkalinities earlier end-points are attained on account of the tendency of Sb^{+3} to oxidize by atmospheric oxygen (*cf.* Table V). The early end-points at higher alkalinities could be overcome by addition of tartaric acid even when $0.01N$ solutions are titrated (*cf.* Table IV).

TABLE II

TITRATION OF 5 ml $0.245N$ POTASSIUM ANTIMONY TARTRATE WITH $0.1422N$ $KMnO_4$ IN THE PRESENCE OF TELLURIC ACID

Alkalinity	*Normality of Sb^{+3}*	*Normality of $KMnO_4$*	*Max. inflection per 0.1 ml $KMnO_4$ mV*	*Theoretical end-point ml*	*Exptl. end-point ml*	*Error %*
$1N$ NaOH	$0.243N$	$0.1083N$	119	18.70	18.68	−0.1
$1.5N$,,	$0.245N$	$0.1422N$	77	14.37	14.38	+0.03
$2N$,,	$0.243N$	$0.1083N$	260	18.70	18.74	+0.2
$2.3N$,,	$0.245N$	$0.1422N$	317	14.37	14.35	−0.14
$3N$,,	,,	,,	213	18.70	18.60	−0.8
$1N$,,	$0.1715N$	$0.1083N$	229	9.35	9.37	+0.2
$2.5N$,,	,,	,,	263	,,	,,	,,
$1N$,,	,,	,,	90	,,	9.38	+0.32
$3N$,,	,,	,,	50	,,	,,	,,

TABLE III

TITRATION OF 10 ml TRIVALENT ANTIMONY IN $2.4N$ HCl WITH $KMnO_4$ IN THE PRESENCE OF TELLURIC ACID

Alkalinity	*Normality of Sb^{+3}*	*Normality of $KMnO_4$*	*Max. inflection per 0.1 ml $KMnO_4$ mV*	*Sb present mg*	*Sb found mg*	*Error %*
$0.4N$ NaOH	$0.1108N$	$0.1422N$	79	67.455	64.588	−4.25
$1N$,,	,,	,,	288	,,	66.726	−1.08
$1.5N$,,	,,	,,	329	,,	66.874	−1.01
$2N$,,	,,	,,	386	,,	66.010	−2.16
$0.5N$,,	$0.01108N$	$0.01422N$	104	6.746	6.735	−0.15
$1N$,,	,,	,,	222	,,	6.654	−1.37
$1.5N$,,	,,	,,	113	,,	6.665	−1.20
$0.25N$,,	$0.001108N$	$0.001422N$	37	0.675	0.6725	−0.37
$0.5N$,,	,,	,,	72	,,	0.678	+0.45

The above results indicate that trivalent antimony could be titrated by $KMnO_4$ to yield good results (except in presence of much chloride) if the reaction is performed in presence of telluric acid when the alkali concentration is kept as low as 0.1*N*-0.5*N*. The alkali concentration could however be raised above this limit if tartaric acid is present in the reaction medium.

TABLE IV

TITRATION OF TRIVALENT ANTIMONY IN HCl WITH POTASSIUM PERMANGANATE IN THE PRESENCE OF TARTARIC ACID AND TELLURIC ACID

Alkalinity	*Max. inflection per 0.1 ml $KMnO_4$ mV*	*Theoretical end-point ml*	*Experimental end-point ml*	*Error %*
Titration of 5.0 ml 0.1084*N* $SbCl_3$ with 0.1083*N* $KMnO_4$				
0.8*N* NaOH	50	8.35(32.57 mg Sb)	8.55 (33.42 mg Sb)	+2.40
1.6*N* ,,	20	,, ,, ,,	8.45 (33.03 ,,)	+1.20
2*N* ,,	80	,, ,, ,,	8.40 (32.84 ,,)	+0.62
2.5*N* ,,	180	,, ,, ,,	8.35 (32.58 ,,)	nil
3*N* ,,	169	,, ,, ,,	,, ,, ,,	,,
Titration of 5.0 ml 0.01084*N* $SbCl_3$ with 0.01083*N* $KMnO_4$				
1*N* NaOH	40	8.35 (3.26 mg Sb)	8.40 (3.28 mg Sb)	+0.61
1.5*N* ,,	26	,, ,, ,,	8.35 (3.26 ,,)	nil
2*N* ,,	40	,, ,, ,,	,, ,, ,,	,,
2.5*N* ,,	40	,, ,, ,,	,, ,, ,,	,,
3*N* ,,	20	,, ,, ,,	,, ,, ,,	,,

TABLE V

TITRATION OF TRIVALENT ANTIMONY IN 0.2*N* NaOH WITH 0.1422*N* $KMnO_4$

Alkalinity	*Vol. and normality of Sb^{+3}*	*Max. inflection per 0.1 ml $KMnO_4$ mV*	*Theoretical end-point ml*	*Exptl. end-point ml*	*Error %*
0.25*N* NaOH	10 ml 0.032*N*	221	3.75	3.74	−0.27
0.5*N* ,,	,, 0.0348*N*	396	4.08	4.07	−0.24
1*N* ,,	25 ml 0.028*N*	279	8.20	8.13	−0.85
1.5*N* ,,	,, ,,	232	,,	8.03	−2.07
2*N* ,,	10 ml 0.0348*N*	255	4.08	3.90	−4.41

TABLE VI

TITRATION OF $KMnO_4$ WITH TRIVALENT ANTIMONY IN THE PRESENCE OF Ba^{+2}

Alkalinity	*5% Ba^{+2} ml*	*Max. inflection per 0.1 ml Sb^{+3} mV*	*Theoretical end-point ml*	*Exptl. end-point ml*	*Error %*
Titration of 10 ml 0.0711*N* $KMnO_4$ with 0.056*N* Sb^{+3} (in alkali)					
1*N* NaOH	10	157	2.53	3.97	+56.91
1.5*N* ,,	10	106	,,	4.31	+70.36
Titration of 20 ml 0.0355*N* $KMnO_4$ with 0.028*N* Sb^{+3} (in alkali)					
0.5*N* NaOH	10	129	5.08	9.46	+86.22
1*N* ,,	8	45	,,	8.15	+60.43
Titration of 20 ml 0.00711*N* $KMnO_4$ with 0.007*N* Sb^{+3} (in alkali)					
0.2*N* NaOH	5	69	4.06	7.44	+83.25
1*N* ,,	5	65	,,	7.80	+92.12

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Reduction of permanganate with trivalent antimony in the presence of Ba^{+2} ions

In contradistinction from arsenic, reduction of permanganate with trivalent antimony could not be checked at the manganate state even in the presence of a large concentration of Ba^{+2} ions. Reduction passes preferentially to MnO_2 owing to the strong reducing power of Sb^{+3}. As may be seen from the data in Table VI the end-points are attained later than the theoretical values and the errors are very high, amounting in some cases to 90%, even when the reactivities of the reactants are decreased by dilution.

Reduction of permanganate by trivalent antimony in the absence of Ba^{+2} ions

In the absence of Ba^{+2} ions reduction of permanganate by trivalent antimony passes directly to the MnO_2 stage. The process of reduction takes place quantitatively in the presence of 2-3*N* NaOH, when Sb^{+3} is applied in the form of $SbCl_3$ and the acidity of the titrant is 2.4*N* with respect to HCl (*cf.* Table VII).

Better results were obtained in the presence of telluric acid and when $SbCl_3$ was applied as the titrant. When on the other hand potassium antimony tartrate solution is used, erroneous results were obtained. The end-points were always attained earlier than the theoretical ones owing to the interference of the tartrate radical (*cf.* Table VIII).

With the $SbCl_3$ solutions in HCl the alkali concentrations could be varied from 2-3*N* without having an appreciable effect on the result. When the concentration of the reactants was halved, the results obtained were equally as good as with the 0.1*N* solutions. At still lower concentrations the end-points were attended with considerable errors. On the other hand, less erroneous results were obtained if a solution of Sb^{+3} in 0.2*N* NaOH was applied as titrant and when the concentration of the reactants was 0.01*N*. In this case also the errors became considerable on diluting the reactants to 0.001*N*.

The titration curves obtained under these conditions (Fig. 2) are smooth and characterized by sharp inflections at the end-points. The reaction occurs rapidly at the beginning of the titration but takes 2-5 min at the end-point.

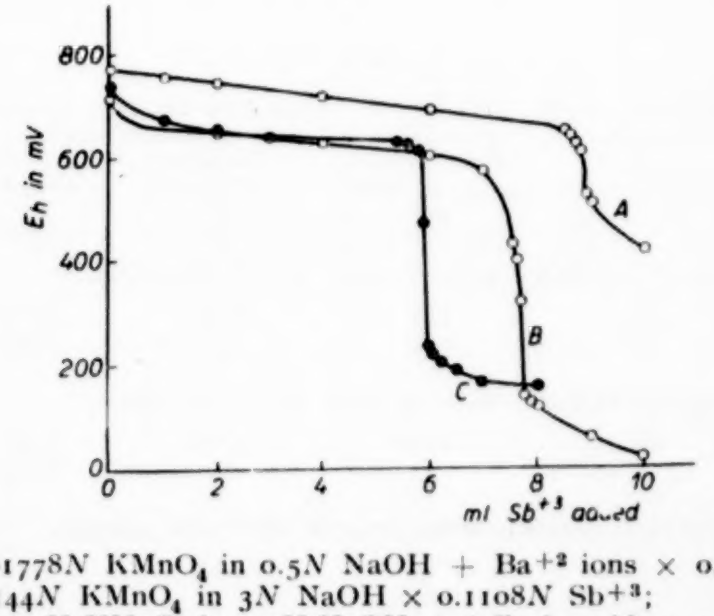

Fig. 2. (A) 20 ml 0.01778*N* $KMnO_4$ in 0.5*N* NaOH + Ba^{+2} ions × 0.14*N* $NaSbO_2$;
(B) 10 ml 0.144*N* $KMnO_4$ in 3*N* NaOH × 0.1108*N* Sb^{+3};
(C) 10 ml 0.1099*N* $KMnO_4$ in 1.7*N* NaOH + telluric acid × 0.1108*N* Sb^{+3}.

TABLE VII

TITRATION OF $KMnO_4$ WITH TRIVALENT ANTIMONY IN ABSENCE OF TELLURIC ACID OR Ba^{+2}

Alkalinity	*Max. inflection per 0.1 ml Sb^{+3} mV*	*Theoretical end-point ml*	*Exptl. end-point ml*	*Error %*
Titration of 10 ml 0.1422*N* $KMnO_4$ with 0.1108*N* $SbCl_3$ in 2.5*N* HCl				
2.2*N* NaOH	206	7.70	7.73	+0.39
2.5*N* ,,	181	,,	7.77	+0.91
3*N* ,,	175	,,	7.72	+0.26

TABLE VIII

TITRATION OF $KMnO_4$ WITH Sb^{+3} IN PRESENCE OF TELLURIC ACID AND ABSENCE OF Ba^{+2}

Alkalinity	*Max. inflection per 0.1 ml Sb^{+3} mV*	*Theoretical end-point ml*	*Exptl. end-point ml*	*Error %*
Titration of 10 ml 0.1099*N* $KMnO_4$ with 0.1108*N* $SbCl_3$ in 2.4*N* HCl				
1.5*N* NaOH	240	5.95	5.93	−0.34
2*N* ,,	315	,,	5.95	nil
3*N* ,,	138	,,	,,	,,
2.5*N* ,,	132	,,	5.90	−0.84
Titration of 10 ml 0.122*N* $KMnO_4$ with 0.245*N* potassium antimony tartrate				
1*N* NaOH	178	6.96	6.20	−10.92
2*N* ,,	186	3.48	3.30	− 5.17
3*N* ,,	159	3.48	3.20	− 8.05
Titration of 10 ml 0.05495*N* $KMnO_4$ with 0.0554*N* $SbCl_3$ in 2.4*N* HCl				
1.75*N* NaOH	155	5.95	5.95	nil
2.5*N* ,,	185	,,	5.97	+0.33
Titration of 10 ml 0.01099*N* $KMnO_4$ with 0.01108*N* $SbCl_3$ in 2.4*N* HCl				
1.5*N* NaOH	181	5.95	5.55	− 6.72
3*N* ,,	124	,,	5.25	−11.76
Titration of 10 ml 0.01422*N* $KMnO_4$ with 0.014*N* $NaSbO_2$ in 0.225*N* NaOH				
1.5*N* NaOH	197	6.09	6.23	+2.30
1.6*N* ,,	134	,,	6.22	+2.13

Estimation of antimony by oxidation with permanganate and back titrating excess oxidant with monovalent thallium

From the above results it is apparent that a scheme depending upon the reaction of permanganate with trivalent antimony in presence of Ba^{+2} would not give good results, on account of the partial reduction of $KMnO_4$ to the manganese dioxide. For this reason we limited our experiments to the reaction in the presence of telluric acid. Under these conditions, reduction of $KMnO_4$, both by trivalent antimony and the monovalent thallium used for the subsequent titration, always proceeds to the quadrivalent manganese stage[13].

The method consists in adding the Sb^{+3} solution dropwise and while continuously stirring to the permanganate-telluric acid mixture, in presence of 1-2*N* NaOH, followed by titrating the excess of oxidant with monovalent thallium. Owing to the rapidity of the reaction, the excess $KMnO_4$ can be titrated immediately after mixing with the Sb^{+3} solution.

As may be seen from Table IX, the method yields good results and can be applied both for the estimation of large amounts of antimony as high as 13 mg and of small quantities as low as 0.67 mg with an error not exceeding 0.55%.

TABLE IX

DETERMINATION OF Sb^{+3} USING Tl^{+} FOR BACK TITRATING EXCESS $KMnO_4$ IN THE PRESENCE OF TELLURIC ACID

$KMnO_4$ = 5 ml 0.1111*N* Tl^{+} = 0.0334*N* NaOH = 1-2*N*

Vol. and normality of Sb^{+3} *solution*	*Sb added* *mg*	*Sb found* *mg*	*Error* %
0.50 ml 0.1108*N*	3.373	3.377	+0.12
1 ,, ,,	6.746	6.743	−0.44
1.5 ,, ,,	10.119	10.125	+0.058
2 ,, ,,	13.492	13.488	−0.030
5 ,, 0.02216*N*	6.746	6.743	−0.44
7.5 ,, ,,	10.119	10.125	+0.058
10 ,, ,,	13.492	13.488	−0.030
1 ,, 0.01108*N*	0.675	0.674	−0.20
3 ,, ,,	2.024	2.023	−0.55
5 ,, ,,	3.373	3.377	+0.12
10 ,, ,,	6.746	6.743	−0.44
15 ,, ,,	10.119	10.125	+0.058

SUMMARY

Titration of Sb^{+3} with $KMnO_4$ gives good results in the presence of telluric acid if the alkali concentration is kept below 0.5*N*. At higher alkalinities early end-points are attained except in the presence of tartaric acid. In the absence of telluric acid reduction of MnO_4^- at higher alkalinities than 0.5*N* NaOH gives Mn_2O_3. On titrating $KMnO_4$ with trivalent antimony the former is reduced to MnO_2. Quantitative results are obtained in the presence of NaOH and when telluric acid is present in the reaction medium. Reduction could not be checked at the manganate state in the presence of Ba^{+2} ions.

The method consisting in oxidation of Sb^{+3} with excess $KMnO_4$, in the presence of telluric acid and 1-2*N* NaOH followed by titrating back the excess of oxidant, with Tl^{+} gives accurate results. Amounts of Sb as low as 0.67 mg could be estimated in this way.

RÉSUMÉ

Le titrage de Sb^{+3} au moyen de $KMnO_4$ donne de bons résultats, en présence d'acide tellurique, si la concentration en hydroxyde alcalin est inférieure à 0.5*N*. Pour des alcalinités plus fortes, les points finaux sont atteints trop rapidement, sauf si l'on est en présence d'acide tartrique. En l'absence d'acide tellurique, la réduction du permanganate donne Mn_2O_3, pour des concentrations en NaOH supérieures à 0.5*N*. Lorsqu'on titre $KMnO_4$ par l'antimoine(III), il y a formation de MnO_2. En présence de NaOH et d'acide tellurique les résultats sont quantitatifs. La réduction ne peut pas être arrêtée au stade manganate, en présence d'ions Ba^{+2}.

La méthode de dosage de l'antimoine(III), par oxydation au moyen de $KMnO_4$, en présence d'acide tellurique et de NaOH 1 à 2*N*, puis par titrage de l'excès de $KMnO_4$ par le thallium(I), donne des résultats précis. On peut doser ainsi jusqu'à 0.67 mg de Sb.

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ZUSAMMENFASSUNG

Die Titration von Sb^{+3} mit $KMnO_4$ in Anwesenheit von Tellursäure gibt gute Resultate wenn die Alkalikonzentration unter 0.5*N* gehalten wird. Ist diese höher, so werden die Endpunkte zu früh erreicht, ausgenommen bei Anwesenheit von Weinsäure. Bei Abwesenheit von Tellursäure und bei Alkalikonzentrationen oberhalb 0.5*N* ergibt die Reduktion von MnO_4^-, Mn_2O_3. Wenn man $KMnO_4$ mit dreiwertigem Antimon titriert, wird Ersteres zu MnO_2 reduziert. Quantitative Resultate werden bei Anwesenheit von NaOH und Tellursäure im Reaktionsmedium erhalten. Bei Anwesenheit von Ba^{+2}-Ionen kann die Reduktion nicht im Manganat-Stadium aufgehalten werden.

Die Methode, die auf der Oxydation von Sb^{+3} mit einem Überschuss von $KMnO_4$ in Anwesenheit von Tellursäure und 1-2*N* NaOH mit nachfolgender Rücktitration des Oxydationsmittels durch Tl^+ beruht, ergibt genaue Resultate. Geringe Mengen von Sb (0.67 mg) können auf diese Weise bestimmt werden.

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THE DETERMINATION OF COPPER USING THE SILVER REDUCTOR

by

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The development of copper-containing arsenical wood preservatives has created the need for a rapid routine method for determining this metal. These preservative mixtures contain in addition to copper: zinc, arsenic and chromate. The standard iodometric method cannot be easily applied in this case owing to the presence of the sexivalent chromium. The electrolytic method used for the analyses of preservatives of the copper chromate type cannot be used without special conditions owing to the presence of arsenic and zinc. It was therefore decided to attempt to apply the silver reductor method of BIRNBAUM AND EDMONDS[1].

In this method copper in 2*N* HCl is passed through a Walden silver reductor and the reduced copper is collected under ferric alum solution. The cuprous copper reduces an equivalent amount of ferric iron and the ferrous iron thus formed is titrated with standard ceric sulphate using "ferroin" as the indicator.

The results given by BIRNBAUM AND EDMONDS show that the method gives excellent results in the determination of 150-200 mg of copper. It has been found, however, that for quantities in the range 5-20 mg of copper consistently low results are obtained. This appears to be due to the fact that during the titration temporary excesses of ceric ion cause the indicator to change to the oxidized form and the reduced colour is restored rather slowly (particularly in the presence of excess ferric iron) tending to lead to undertitration. This view is supported by the observation that the discrepancies become larger with decreasing amounts of copper.

Because the technique afforded a neat and direct approach to the copper analysis it was decided to see, whether by suitable modification a more reliable method could be developed. It has been found that by collecting the reduced copper in standard dichromate solution and determining the excess dichromate by the usual ferrous sulphate-dichromate titration, using barium diphenylamine sulphonate as indicator, a very satisfactory routine procedure for determining copper was obtained.

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* Investigations were made at Research Department, Boliden Mining Co., Skelleftehamn, Sweden.

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METHOD

Reagents

$0.02N$ $K_2Cr_2O_7$
$0.05N$ $FeSO_4$
0.3% Ba diphenylamine sulphonate
Conc. H_3PO_4
1:1 H_2SO_4
$2N$ HCl
$4N$ HCl

Procedure

1. Prepare and set up a Walden silver reductor[2].
2. Place the sample containing about 5-20 mg Cu together with an equal volume of $4N$ HCl in the reductor reservoir.
3. Allow the solution to pass through the reductor at about 30 ml/min.
4. Collect the reduced copper solution in a 400 ml beaker containing 25.0 ml of dichromate, 10 ml H_3PO_4, 10 ml of 1:1 H_2SO_4 diluted to 200 ml with distilled water. This solution should be stirred gently and the reductor tube should reach nearly to the bottom of the beaker.
5. Wash the reductor tube free of copper with several portions of $2N$ HCl allowing each portion to drain to the top of the silver in the column before adding the next. The entire volume of HCl used should equal 100 ml of $2N$ HCl.
6. When the reduction is complete remove the solution, washing the end of the column with distilled water.
7. Add 20 ml of ferrous sulphate solution and back-titrate the excess ferrous solution with dichromate using Ba diphenylamine sulphonate as indicator. The end-point is violet. Titre = A ml.
8. Carry out a blank determination using the same quantities of all reagents. This gives the reductor blank (about 0.1 ml of $0.02N$ dichromate) + ferrous sulphate equivalent. Titre = B. Then $1.271\ (A + 25 - B)$ = mg Cu.

TABLE I

Cu taken *mg*	*Cu found* *mg*
4.00	4.07
10.00	10.07
20.00	20.12

TABLE II

Approximate composition of mixture, g/litre				*Cu*	*Cu*
Cu	Cr^{+6}	As_2O_3	*Zn*	*Method (a)*	*New Method (b)*
0.7	0.9	2.2		0.72	0.71
0.3	1.15	3.3	0.8	0.33	0.33
0.3	0.3	2.0	0.3	0.33	0.31
0.7	0.7	4.0	0.7	0.70	0.69
1.3	1.3	6.7	1.3	1.33	1.32
1.5	1.5	8.0	1.5	1.50	1.54

(a) Cu determined by precipitation with thioacetamide, oxidation and solution in HNO_3 and titration with KI and thiosulphate.
(b) Reductor method.

The figures given above show that the method gives good agreement with the present routine procedure using thioacetamide.

Notes

1. The strength of the reagents may be increased if micro burettes are used.
2. The dichromate used to oxidize the cuprous copper should be equivalent to at least twice the anticipated copper content. For amounts of copper in excess of 20 mg the dichromate should be increased proportionately.
3. Interferences of the common metals. Only Fe, Mo, U, V, interfere being reduced to lower valency states in the reductor. Of these interferences that of iron is the only serious objection to the method. However, owing to the insolubility of Fe^{+3} arsenate in wood-preserving solutions this interference is not serious especially if the solutions are filtered before analysis.

The results obtained by the method are given in Tables I and II.

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SUMMARY

A new method is described for the routine determination of copper using a silver reductor.

RÉSUMÉ

L'auteur décrit une nouvelle méthode permettant le dosage du cuivre au moyen d'un réducteur à l'argent.

ZUSAMMENFASSUNG

Es wird eine neue Methode zur Bestimmung von Kupfer mit einem Silberreduktionsmittel beschrieben.

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ÉTUDES SUR LA DÉTECTION, LA CARACTÉRISATION ET LE DOSAGE DES ALDÉHYDES

II. DÉRIVÉS FORMÉS PAR RÉACTION AVEC LE BIS- (*p*-MÉTHOXY-BENZYLAMINO)-1.2 ÉTHANE OU BIS-PHÉNYLAMINO-1.2 ÉTHANE

par

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BILLMAN, HO ET CASWELL[1] ont recommandé pour la caractérisation des aldéhydes leur condensation avec le bis-(*p*-méthoxybenzylamino)-1.2 éthane, par laquelle des bis-(*p*-méthoxybenzyl)-1.3 alcoyl(ou aryl)-2 imidazolidines sont formées. Ces dérivés ont l'avantage sur les dimédonates, qu'aucune anhydrisation ultérieure ne peut prendre place. De plus, les dérivés étant des amines tertiaires bivalentes, nous nous sommes proposés d'examiner si l'on peut déterminer leurs poids moléculaires par titrage de leurs solutions dans l'acide acétique cristallisable avec l'acide perchlorique 0.1*N* dans le même solvant, potentiométriquement ou visuellement (indicateur: violet cristallisé), malgré l'indication de BILLMAN, HO ET CASWELL, que les imidazolidines sont lentement hydrolysées par l'acide chlorhydrique à 10%.

Le Tableau I montre, que la détermination est en fait possible, une molécule de l'imidazolidine substituée exigeant deux (ou pour les imidazolidines pyridyl-substituées trois) molécules d'acide, mais l'exactitude de la détermination du poids moléculaire de l'aldéhyde n'est pas grande, car il faut retrancher 282.4 ($C_{18}H_{22}ON_2$) du poids moléculaire du dérivé ($C_{19}H_{23}O_2N_2R$) pour trouver le poids moléculaire de l'aldéhyde RCHO. Prévoyant la précision 1% pour le titrage, l'erreur numérique peut être 3 à peu près, ce qui, pour les aldéhydes inférieurs, signifie une erreur considérable.

Plus récemment, WANZLICK ET LÖCHEL[2] ont proposé la préparation des imidazolidines substituées pour caractériser les aldéhydes en les condensant avec le bis-phénylamino-1.2 éthane. Nous avons préparé les diphényl-1.3 alcoyl(ou aryl)-2 imidazolidines de nos aldéhydes témoins[3], et nous trouvons pour les aldéhydes examinés auparavant par WANZLICK ET LÖCHEL les points de fusion indiqués par eux. De plus, nous en indiquons quelques-uns non mentionnés par WANZLICK ET LÖCHEL.

Espérant que ces imidazolidines, des poids moléculaires desquelles il ne faut retrancher que 192.1 ($C_{15}H_{15}N_2R—C_{14}H_{14}N_2 + O$) pour arriver au poids moléculaire de l'aldéhyde, soient aussi bien titrables que les imidazolidines mentionnées plus haut, nous les avons dissoutes dans l'acide acétique cristallisable pour en faire le titrage avec l'acide perchlorique dans le même solvant.

TABLEAU

BIS-(*p*-MÉTHOXYBENZYL)-

Aldéhyde	*R*	*Poiut de fusion*	
		Trouvé	*Litt.*
Formique (Paraforme)	H	29.5-30°	30°
Acétique	CH_3	82-82.5°	76-77°
Isobutyrique	$(CH_3)_2CH$	44.5-45°	huile
Triméthylacétique	$(CH_3)_3C$	88.5-89°	—
Heptaldéhyde	C_6H_{13}	huile	huile
Benzaldéhyde	C_6H_5	96°	93°
o-Tolylaldéhyde	$2\text{-}CH_3C_6H_4$	67-67.5°	—
Diméthyl-2.6 benzaldéhyde	$2.6\text{-}(CH_3)_2C_6H_3$	81°	—
Furfural	$OC_4H_3\text{-}2$	75.5-76°	76°
Thiénal-2	$SC_4H_3\text{-}2$	93-94°	—
Pyridylaldéhyde-2	$NC_5H_4\text{-}2$	—	—
Pyridylaldéhyde-3	$NC_5H_4\text{-}3$	121°	—
Pyridylaldéhyde-4	$NC_5H_4\text{-}4$	113.5°	—

* demandant 3 molécules d'acide perchlorique par molécule d'imidazolidine.

TABLEAU

DIPHÉNYL-1.3 ALCO

Aldéhyde	*R*	*Point de fusion*	
		Trouvé	*Litt.*
Formique (Paraforme)	H	125-126°	126°
Acétique	CH_3	102-103°	102.5°
Isobutyrique	$(CH_3)_2CH$	97-98°	—
Triméthylacétique	$(CH_3)_3C$	—[2])	—
Heptaldéhyde	C_6H_{13}	77-78°	79°
Benzaldéhyde	C_6H_5	135-136°	137°
o-Tolylaldéhyde	$2\text{-}CH_3C_6H_4$	126-127°	127.5°
Diméthyl-2.6 benzaldéhyde	$2.6\text{-}(CH_3)_2C_6H_3$	—[2])	—
Furfural	$OC_4H_3\text{-}2$	136°	137°
Thiénal-2	$SC_4H_3\text{-}2$	117-118°	—
Pyridylaldéhyde-2	$NC_5H_4\text{-}2$	173.5-174.5°	—
Pyridylaldéhyde-3	$NC_5H_4\text{-}3$	145-146°	—
Pyridylaldéhyde-4	$NC_5H_4\text{-}4$	149.5-150.5°	—

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[1] Titrage impossible.

[2] Aucune imidazolidine ne se forme.

COYL(OU ARYL)-2 IMIDAZOLIDINES

E			C	H	N	S
Calc.	Trouvé					
156.2	157		—	—	—	—
163.2	164.7		—	—	—	—
177.2	176.1	calc.	74.54	8.53	7.90	—
		trouvé	75.35	8.71	7.61	—
184.2	184.7	calc.	74.96	8.75	7.60	—
		trouvé	75.25	8.54	7.52	—
—	—		—	—	—	—
194.2	195.1		—	—	—	—
201.2	200.3	calc.	77.58	7.51	6.96	—
		trouvé	77.50	7.51	6.86	—
207.3	212	calc.	77.84	7.74	6.73	—
		trouvé	77.80	7.86	6.61	—
189.2	188.0		—	—	—	—
197.3	196.9	calc.	70.02	6.64	7.00	8.02
		trouvé	70.10	6.77	7.19	8.21
—	—		—	—	—	—
129.8*	133.9	calc.	74.01	6.99	10.79	—
		trouvé	73.50	6.89	10.56	—
129.8*	134.7	calc.	74.01	6.99	10.79	—
		trouvé	74.05	7.15	10.46	—

OU ARYL)-2 IMIDAZOLIDINES

E			C	H	N	S
Calc.	Trouvé					
112.2	—[1])		—	—	—	—
119.2	120.8		—	—	—	—
133.2	132.5	calc.	81.16	8.33	10.52	—
		trouvé	91.10	8.32	10.52	—
—	—		—	—	—	—
154.2	154.4		—	—	—	—
150.2	152.6		—	—	—	—
157.2	156.5		—	—	—	—
—	—		—	—	—	—
145.2	—[3])		—	—	—	—
153.2	—[3])	calc.	74.47	5.92	9.14	10.46
		trouvé	74.30	5.94	9.17	10.52
100.4[4])	101.4	calc.	79.70	6.36	13.94	—
		trouvé	79.50	6.15	13.96	—
100.4[4])	102.2	calc.	79.70	6.36	13.94	—
		trouvé	79.70	6.25	14.15	—
100.4[4])	102.0	calc.	79.70	6.36	13.94	—
		trouvé	79.50	6.39	13.98	—

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[3] Titrage impossible, le liquide prenant une couleur rouge foncé.

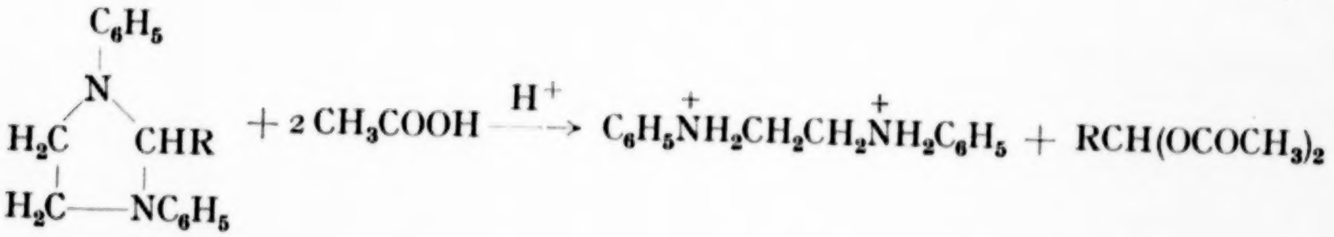
[4] Demandant 3 molécules d'acide perchlorique par molécule d'imidazolidine.

Pendant le titrage potentiométrique de ces imidazolidines nous avons fait quelques observations assez remarquables: le potentiel tarde à s'établir, de sorte qu'il faut attendre quelques minutes jusqu'à une heure après chaque addition d'acide perchlorique pour faire la lecture du potentiel. En même temps une substance cristalline se dépose, évidemment un perchlorate.

Un examen du précipité a montré, que c'est le perchlorate du bis-phénylamino-1.2 éthane, de sorte que l'imidazolidine a été décomposée en bis-phénylamino-1.2 éthane et aldéhyde, ce qui explique, que le potentiel ne s'établit pas instantanément. Toutefois, la décomposition est le plus souvent suffisamment rapide pour permettre le titrage visuel; seulement dans le cas du formaldéhyde nous avons trouvé une décomposition si lente de la diphényl-1.3 imidazolidine, que le titrage est rendu impossible.

Wanzlick et Löchel indiquent, que les imidazolidines sont hydrolysées en les agitant pendant une demi-heure avec de l'acide chlorhydrique à 10%. Nos expériences montrent, que même des quantités minimes d'acide perchlorique suffisent pour provoquer la dissociation, le solvant étant l'acide acétique cristallisable. Le solvant ne provoque aucune dissociation, car d'une solution de la triphényl-1.2.3 imidazolidine dans l'acide acétique cristallisable on peut, après un repos de deux heures, retrouver la substance inaltérée après dilution par l'eau et neutralisation de l'acide acétique. Une solution analogue, à laquelle la quantité calculée d'acide perchlorique a été ajoutée, donne après un repos d'une demi-heure le bis-phénylamino-1.2 éthane avec un rendement à peu près quantitatif.

Le mélange réactionnel étant anhydre, la réaction doit être:


C_6H_5
N
H_2C
CHR
H_2C
NC_6H_5
$+ 2\,CH_3COOH \xrightarrow{H^+} C_6H_5\overset{+}{N}H_2CH_2CH_2\overset{+}{N}H_2C_6H_5 + RCH(OCOCH_3)_2$

Le titrage des imidazolidines étant accompagné par la libération de l'aldéhyde ou de son diacétate, il va sans dire, que les dérivés des aldéhydes sensibles vis-à-vis de l'acide perchlorique (p. ex. le furfural, le thiénal-2) ne se laissent pas titrer, car ces aldéhydes forment sous l'influence de l'acide perchlorique des produits de décomposition fortement colorés.

Avec les bis-(*p*-méthoxybenzyl) imidazolidines nous n'avons pas trouvé cette difficulté en titrant les dérivés du furfural ou du thiénal-2.

Il semble donc que la stabilité de l'anneau imidazolidinique dépend des substituants présents, les substituants aromatiques diminuant la stabilité plus que les substituants de caractère aliphatique comme le radical *p*-méthoxybenzyl[4].

Pour vérifier la stabilité relative des bis-(*p*-méthoxybenzyl) imidazolidines, nous avons répété l'expérience que nous venons de décrire, cette fois en prenant la bis-(*p*-méthoxybenzyl)-1.3 phényl-2 imidazolidine. Après addition de la quantité calculée d'acide perchlorique la solution fut abandonnée pendant une demi-heure et ensuite diluée par l'eau et neutralisée avec de l'hydroxyde de sodium. L'imidazolidine substituée fut trouvée avec un rendement à peu près quantitatif.

PARTIE EXPÉRIMENTALE*

Les bis-(*p*-méthoxybenzyl)-1.3 alcoyl (ou aryl)-2 imidazolidines furent préparés en suivant les indications de BILLMAN, HO ET CASWELL[1]. Dans le Tableau I sont indiqués les points de fusion trouvés par nous et ceux indiqués dans la littérature, ainsi que les poids moléculaires calculés et trouvés par titrage avec l'acide perchlorique en dissolvant 0.0005 moles de l'imidazolidine dans 20-25 ml d'acide acétique cristallisable et en titrant la solution par une solution d'acide perchlorique 0.1*N* dans l'acide acétique cristallisable. De plus, nous indiquons l'analyse élémentaire pour les dérivés que nous n'avons pas trouvés dans la littérature.

Le Tableau II contient les données correspondantes pour les diphényl-1.3 alcoyl(ou aryl)-2 imidazolidines.

L'exactitude de la détermination du point d'équivalence semble être inférieure à l'exactitude habituelle des méthodes acidimétriques, dû sans doute au fait que la ,,solvolyse" ne se produit qu'au fur et à mesure de l'addition de l'acide perchlorique. Pendant le titrage, l'indicateur vire du violet bleuâtre au jaune en passant par le bleu, puis le vert.

En préparant ces dérivés, nous avons suivi les indications de WANZLICK ET LÖCHEL[2].

Instabilité de la triphényl-1.2.3 imidazolidine. 0.6 g de triphényl-1.2.3 imidazolidine est dissous dans 40 ml d'acide acétique cristallisable. Après un repos de 2 heures, 25 g de glace sont ajoutés, et la solution est neutralisée par de l'hydroxyde de sodium 10*N*, précipitant une substance qui, après filtrage, est recristallisée dans l'éthanol. Rendement 0.5 g de point de fusion 135-136° C. C'est donc l'imidazolidine inaltérée qui est ainsi retrouvée, avec un rendement de 83 %.

0.6 g de triphényl-1.2.3 imidazolidine est dissous dans 25 ml d'acide acétique cristallisable, et 40.2 ml d'acide perchlorique 0.1*N* dans l'acide acétique cristallisable sont ajoutés, précipitant une substance, qui après un repos de 30 minutes est isolée par décantation du solvant. Le résidu est dissous dans l'eau. Par addition d'hydroxyde de sodium une substance précipite, qui est isolée par filtrage, lavée par de l'eau, recristallisée dans l'éthanol et séchée. Rendement 0.35 g de point de fusion 65-67° C. On a donc retrouvé le bis-phénylamino-1.2 éthane avec un rendement de 83%.

Stabilité de la bis-(p-méthoxybenzyl)-1.3 phényl-2 imidazolidine. 0.8 g de bis-(*p*-méthoxybenzyl)-1.3 phényl-2 imidazolidine est dissous dans 30 ml d'acide acétique cristallisable, et 40.5 ml d'acide perchlorique 0.1*N* dans l'acide acétique cristallisable sont ajoutés. Après un repos de 30 minutes, 40-50 g de glace sont ajoutés, et la solution est neutralisée par l'hydroxyde de sodium 10*N*, précipitant une substance, qui est recueillie par filtrage, lavée par de l'eau et recristallisée dans l'éthanol. Rendement 0.65 g ou 80% avec point de fusion 96° C. L'imidazolidine substituée n'a donc pas été décomposée pendant le titrage.

Nous tenons à remercier LAURITS ANDERSENS FOND et OTTO MØNSTEDS FOND pour des subventions, qui ont permis à l'un de nous (I.G.K.A.) de prendre part à ces recherches.

RÉSUMÉ

La condensation d'une série sélectionnée d'aldéhydes avec le bis-(*p*-méthoxybenzylamino)-1.2 éthane et le bis-phénylamino-1.2 éthane a été examinée. Les indications de BILLMAN, HO ET CASWELL[1] et de WANZLICK ET LÖCHEL[2] ont été vérifiées, et quelques imidazolidines 1.2.3-trisubstituées nouvelles ont été préparées.

Les bis-(*p*-méthoxybenzyl)-1.3 alcoyl(ou aryl)-2 imidazolidines sont des bases suffisamment fortes pour permettre leur titrage avec l'acide perchlorique dans l'acide acétique cristallisable, exigeant deux ou, dans le cas des imidazolidines pyridyl-substituées, trois molécules d'acide perchlorique par molécule d'imidazolidine.

En essayant de titrer les diphényl-1.3 alcoyl(ou aryl)-2 imidazolidines, on a constaté une "solvolyse" de l'imidazolidine en bis-phénylamino-1.2 éthane, précipitant en diperchlorate et diacétate de l'aldéhyde hydraté. La "solvolyse" n'étant pas instantanée, la précision du titrage n'est pas aussi grande que celle obtenue avec les dérivés proposés par BILLMAN, HO ET CASWELL.

SUMMARY

The condensation of a selected series of aldehydes with 1.2-bis-(*p*-methoxybenzylamino) ethane and with 1.2-bis-phenylamino ethane has been investigated. The results of BILLMAN, HO AND CASWELL[1] and of WANZLICK AND LÖCHEL[2] have been verified and some new 1.2.3-trisubstituted imidazolidines have been prepared.

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* Points de fusion sur des thermomètres tronqués; microanalyses par M. P. HANSEN, Laboratoire de Chimie Organique, Université de Copenhague.

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The 1.3-bis-(*p*-methoxybenzyl)-2-alkyl(or aryl) imidazolidines are sufficiently strong bases to be titrated with perchloric acid in glacial acetic acid solution as dibasic bases (or, for the derivatives of the pyridylaldehydes, as tribasic bases).

The 1.3-diphenyl-2-alkyl(or aryl)-imidazolidines are "solvolysed" under the influence of the perchloric acid into the 1.2-bis-phenylaminoethane and the diacetate of the aldehyde-hydrate. The "solvolysis" not being instantaneous, the precision of the titration is not as good as that obtained in titrating the derivatives recommended by BILLMAN, HO AND CASWELL.

ZUSAMMENFASSUNG

Die Kondensation einer ausgewählten Reihe von Aldehyden mit 1.2-Bis-(*p*-methoxybenzylamino)-äthan und mit 1.2-Bis-phenylamino-äthan wurde untersucht. Die Ergebnisse von BILLMAN, HO UND CASWELL[1] und von WANZLICK UND LÖCHEL[2] wurden bestätigt, und einige neue 1.2.3-trisubstituierte Imidazolidine beschrieben.

Die 1.3-Bis (*p*-methoxybenzyl)-2-alkyl(oder aryl)-imidazolidine sind genügend starke Basen um ihre Titration (als zweibasische oder für die Derivate der Pyridinaldehyde als dreibasische Basen) mit Perchlorsäure in Eisessig zu erlauben.

Die 1.3-Diphenyl-2-alkyl(oder aryl)-imidazolidine werden unter dem Einfluss der Perchlorsäure in Bis-phenylamino-äthan und Diacetat des Aldehydhydrates "solvolysiert". Da die "Solvolyse" nicht momentan ist, wird die Genauigkeit der Titration etwas geringer als diejenige der von BILLMAN, HO UND CASWELL vorgeschlagenen Derivate.

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DIALLYLDITHIOCARBAMIDO-HYDRAZINE AS AN ANALYTICAL REAGENT

PART I. DETERMINATION OF COPPER, NICKEL, ZINC AND LEAD AND SEPARATIONS OF THEIR BINARY MIXTURES

by

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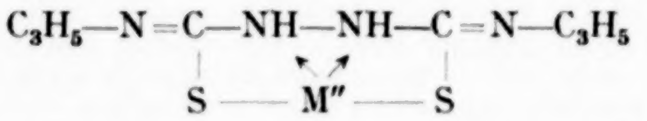
This reagent was used by GUPTA[1] and one of us (K.P.S.S.) for the colorimetric determination of bismuth. The analytical application of the compound C_3H_5-NH-CS-NH-NH-CS-NH-C_3H_5 has been possible because of the presence of potential mercapto groups which come into operation by enolization with the neighbouring amino or imino groups: C_3H_5-N=C(SH)-NH-NH-C(SH)=N-C_3H_5. In its enolic form, the compound acts as a dibasic acid. It has been observed that the reagent in its enolic form, forms insoluble complexes with many bivalent metals like copper, nickel, zinc, lead, *etc.* which are precipitated quantitatively from their solutions under controlled pH values. Copper is precipitated quantitatively between pH 2.5 and 3.5, lead between 5 and 6, nickel between 8 and 9 and zinc between 7.5 and 8.6. These complexes have been found to have definite compositions and to be capable of being directly weighed in a tared Gooch crucible. They have been found to have the general formula,



$$\begin{array}{ccccccccc} C_3H_5- & N= & C & -NH- & & -NH- & C & =N- & C_3H_5 \\ & & | & \searrow & & \swarrow & | & & \\ & & S & - & M'' & - & S & & \end{array}$$

where M″ is a bivalent metal like Cu, Ni, Zn, Pb. Copper and lead compounds were previously described by GUPTA AND SEN SARMA[1]. Nickel and zinc compounds have been prepared and analysed and have been found to have the composition, $Ni(C_8H_{12}N_4S_2).\frac{1}{2}H_2O$, [Ni 19.67, S 21.75, N 18.78]. The half-molecule of water of crystallisation is not eliminated at 105° C and remains intact after drying for several hours; hence, the compound was dried at this temperature and weighed. The zinc compound has the composition $Zn(C_8H_{12}N_4S_2)$, being anhydrous like the corresponding copper and lead compounds, [Zn 22.05, S 22.02, N 19.22]. An alcoholic solution of the reagent was used for precipitations, and since the reagent was only slightly soluble in water, the precipitates were finally washed on the Gooch crucible with acetone in the case of Ni, Zn and Pb, and with methyl alcohol in the case of Cu (the copper compound being slightly soluble in acetone) till free from reagent when tested with bismuth.

The individual determinations of copper, nickel, zinc and lead and separations of the binary mixtures Cu-Ni, Cu-Zn, and Cu-Pb by means of the reagent form the subject matter of the present communication.

EXPERIMENTAL

The reagent was prepared by the method of FREUND AND WISCHEWIANSKY[2].

E. Merck 'Pro analysis' chemicals were used.

Standard burette, pipette, volumetric flasks and one box of calibrated weights were used throughout the experiments.

Determination of copper

A measured volume of the copper solution was taken in a beaker. Dilute ammonia solution was added dropwise till the solution was deep blue. Dilute sulphuric acid was then added till the precipitation of $Cu(OH)_2$ began.

The addition of acid was continued, leaving some $Cu(OH)_2$ undissolved, and the turbidity was just cleared by addition of a dilute solution of citric acid. The solution was diluted to 200 ml and a slight excess of the calcultated quantity of the reagent solution added with constant stirring. The precipitate was allowed to settle for about 2 hours in the cold. It was then washed 2 to 3 times by decantation with cold water, transferred to the crucible and washed finally with methyl alcohol to remove excess reagent. It was then dried at 105° C and weighed as $Cu(C_8H_{12}N_4S_2)$.

TABLE I

No.	**Citric acid* ml	*Wt of copper compound* g	*Cu found* g	*Cu taken* g	pH
1	0.0	0.0718	0.01564	0.01564	3.5
2	0.25	0.1672	0.03641	0.03644	3.1
3	0.5	0.1676	0.03652	0.03644	2.8
4	0.75	0.1665	0.03628	0.03644	2.5
5	1.0	0.1654	0.03605	0.03644	2.0 low
6	1.25	0.1636	0.03571	0.03644	1.8 low
7	1.5	0.1150	0.02505	0.02526	1.6 low
8	0	0.1672	0.03641	0.03644	3.5
9	0	0.2319	0.05051	0.05053	3.5
10	0	0.2866	0.06246	0.06255	3.5

* More than the amount required to just clear the turbidity due to $Cu(OH)_2$.

Determination of nickel

A measured volume of nickel solution was taken in a beaker and the solution was prepared as before. It was then diluted to 200 ml and heated on a water bath. Nickel was precipitated by using a slight excess of the reagent solution. To this solution was then added 1 g of sodium acetate (precipitation may begin here if the amount of nickel is appreciable) and about 1 g of NaOH in solution (0.7 g is generally required for nickel varying from 0.02 g—0.1 g) with constant stirring. It was then allowed to settle on the water bath, filtered, washed with hot water and finally with acetone, dried at 105° C and weighed as $Ni(C_8H_{12}N_4S_2) \cdot \frac{1}{2} H_2O$.

TABLE II

No.	*Weight of Ni compound* g	*Ni found* g	*Ni taken* g
1	0.1143	0.02266	0.02266
2	0.1525	0.03022	0.03021
3	0.2295	0.04550	0.04532
4	0.2667	0.05288	0.05287
5	0.3044	0.06041	0.06042
6	0.3812	0.07558	0.07553

Determination of zinc

The solution was prepared as before. After adding the reagent solution the mixture was heated on a water bath, and 3 g of CH_3COONa followed by a freshly prepared solution of NaOH (about 0.3 g) were added dropwise with continuous stirring. The precipitate was allowed to settle, then filtered on a crucible, washed with acetone, dried at 105° C as before and weighed as $Zn(C_8H_{12}N_4S_2)$.

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TABLE III

No.	*Wt of Zn compound* g	*Zn found* g	*Zn taken* g
1	0.0939	0.02090	0.02087
2	0.1135	0.02527	0.02505
3	0.1324	0.02947	0.02923
4	0.1693	0.03769	0.03758
5	0.1970	0.04163	0.04175
6	0.2257	0.05024	0.05011

Determination of lead

A measured volume of lead solution was taken in a beaker and few drops of bromo-cresol purple indicator were added. The solution was neutralized with dilute ammonia till $Pb(OH)_2$ began to precipitate. A solution of citric acid was then added until the precipitate dissolved, on heating if necessary, and the total quantity diluted to 150 ml. Reagent solution followed by caustic soda solution were then added, with continuous stirring, till the supernatant liquid turned purple. Lead was precipitated as a canary-yellow heavy compound in the cold. It was then allowed to settle for 2 hours, filtered, washed with cold water and finally with acetone, dried at 105° C and weighed as $Pb(C_8H_{12}N_4S_2)$.

TABLE IV

No.	*Wt of Pb compound* g	*Pb found* g	*Pb taken* g
1	0.0955	0.04542	0.04567
2	0.1283	0.06099	0.06090
3	0.1432	0.06807	0.06851

Separation of binary mixture

Cu-Ni separation. Measured volumes of copper and nickel solutions were taken in a 400 ml beaker. The copper was first precipitated from the mixture under suitable conditions. Nickel was estimated in the filtrate by the usual procedure.

TABLE V

No.	*Wt of Cu compound* g	*Wt of Ni compound* g	*Cu taken* g	*Cu found* g	*Ni taken* g	*Ni found* g
1	0.2427	0.1919	0.05213	0.05286	0.03776	0.03840
2	0.0958	0.4543	0.02085	0.02086	0.09064	0.09006
3	0.0719	0.4555	0.01564	0.01566	0.09063	0.09031
4	0.2890	0.2310	0.06256	0.06294	0.04532	0.04580
5	0.3621	0.2685	0.07819	0.07886	0.05287	0.05326
6	0.3589	0.1155	0.07819	0.07816	0.02266	0.02289
7	0.2154	0.1540	0.04692	0.04691	0.03021	0.03053

Cu-Zn separation. Measured volumes of copper and zinc solutions were taken in a beaker, copper was precipitated in the usual way, and from the filtrate zinc was precipitated after raising the pH with sodium acetate and caustic soda as usual.

TABLE VI

No.	*Wt of Cu compound* g	*Wt of Zn compound* g	*Cu taken* g	*Cu found* g	*Zn taken* g	*Zn found* g
1	0.1189	0.1881	0.02606	0.02590	0.04175	0.04185
2	0.1450	0.1686	0.03128	0.03158	0.03758	0.03753
3	0.1685	0.1505	0.03649	0.0369	0.03340	0.03350
4	0.1920	0.1322	0.04170	0.04181	0.02923	0.02938
5	0.2168	0.1131	0.04692	0.04722	0.02505	0.02517
6	0.2401	0.0944	0.05213	0.05229	0.02087	0.02101

Cu-Pb separation. Measured volumes of $Cu(NO_3)_2$ and $Pb(NO_3)_2$ were taken in a beaker and neutralized with dilute ammonia solution. In this solution copper was determined by the usual procedure.

In the filtrate lead was estimated in the usual way after concentration and cooling.

TABLE VII

No.	*Wt of Cu compound* g	*Wt of Pb compound* g	*Cu taken* g	*Cu found* g	*Pb taken* g	*Pb found* g
1	0.2106	0.1597	0.04563	0.04586	0.07612	0.07598
2	0.1059	0.1600	0.02288	0.02306	0.07612	0.07612
3	0.1056	0.1597	0.02288	0.02299	0.07612	0.07598
4	0.1265	0.1120	0.02738	0.02755	0.05328	0.05328
5	0.1684	0.1444	0.03651	0.03667	0.06851	0.06896

SUMMARY

The paper describes the use of diallyldithiocarbamido-hydrazine as an analytical reagent. The reagent precipitates copper, nickel, zinc and lead quantitatively from their solutions under controlled pH values. Copper is precipitated quantitatively between pH 2.5 and 3.5, lead between 5 and 6, zinc between 7.5 and 8.6 and nickel between 8 and 9. These complexes have been found to possess definite compositions and to be capable of being directly weighed in a weighed crucible. The elements have been determined individually and also in their binary mixtures after adjusting the pH values.

RÉSUMÉ

Les auteurs proposent l'emploi de la diallyldithiocarbamido-hydrazine comme réactif analytique. Ce réactif précipite quantitativement le cuivre, le nickel, le zinc et le plomb à divers pH: le cuivre entre 2.5 et 3.5, le plomb entre 5 et 6, le zinc entre 7.5 et 8.6 et le nickel entre 8 et 9. On connaît la constitution de ces composés; ils peuvent être pesés directement dans un creuset de Gooch. On peut ainsi effectuer des dosages de ces éléments, soit individuellement, soit dans des mélanges binaires, en fixant le pH.

ZUSAMMENFASSUNG

Als analytisches Reagens schlagen die Autoren die Anwendung von Diallyldithiocarbamidhydrazin vor. Dieses Reagens fällt Kupfer, Nickel, Zink und Blei bei verschiedenen pH-Werten quantitativ aus, und zwar Kupfer zwischen 2.5 und 3.5, Blei zwischen 5 und 6, Zink zwischen 7.5 und 8.6 und Nickel zwischen 8 und 9. Man kennt die Konstitution dieser Verbindungen; sie können direkt in einem Gooch-Tiegel gewogen werden. Nach dieser Methode können folglich die angeführten Metalle einzeln, oder aus binären Mischungen nach Einstellen des pH-Wertes bestimmt werden.

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OXYGEN IN ORGANIC SUBSTANCES

SOME MODIFICATIONS TO SCHÜTZE-UNTERZAUCHER METHOD

by

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SCHÜTZE[8,9], developed a direct semi-microdetermination of oxygen in organic substances using carbon as a reducing agent and ZIMMERMANN[16] adapted it to a microchemical scale. The organic substance is pyrolized in a stream of purified nitrogen and the gases are passed over carbon at 1000° C, then the carbon monoxide obtained is oxidized by means of iodine pentoxide and the carbon dioxide is determined gravimetrically.

UNTERZAUCHER[11,12,13,14] modified the final step of the method using the determination of iodine that was absorbed in sodium hydroxide solution, and the multiplication process of VIEBÖCH AND BRECHER[15]. This consists in the oxidation of iodine with bromine to iodate, which after addition of formic acid to destroy the excess of bromine, reacts with potassium iodide in acid solution to liberate an amount of iodine corresponding to six times the iodine originally produced in the reaction between carbon monoxide and iodine pentoxide. Sources of error in the method are hydrogen and sulfur compounds formed during the pyrolisis of the sample[1,2,3,7].

The hydrogen is removed by means of a palladium thimble at 350° C[1] and the errors caused by sulfur compounds which are not retained by alkali are avoided using copper at 900° C[5,6,7]. Simultaneous use of both — palladium thimble and copper at 900° C — contributes to minimize errors in the quantitative liberation of iodine. The liberated iodine is fixed in thiosulphate-iodide solution and it is determined amperometrically instead of using the classical starch indicator end-point[14], increasing the sensitivity of the titration. The multiplication process for iodine of VIEBÖCH AND BRECHER[15] is not used. Possible errors of this multiplication process are therefore eliminated. The amperometric titration is more convenient, because it simplifies the method and saves time.

The modifications to SCHÜTZE-UNTERZAUCHER method include therefore the use in the apparatus of both — palladium thimble and copper at 900° C — minimizing the errors due to hydrogen and sulfur compounds in the quantitative liberation of iodine and the subsequent fixation of iodine in thiosulphate-iodide solution with amperometric titration of thiosulphate excess.

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Apparatus

The apparatus is unitized and easy to operate. The reducing valves of nitrogen and hydrogen tanks are connected to the corresponding needle valves by heavy-walled rubber tube. The glass tube used was standard wall 7 to 8 mm O.D. Glass tubing 2 mm I.D. and 8 mm O.D. was used before the ascarite-dehydrite tubes (H_1, H_2), the copper gauze tube (P) and the iodine pentoxide tube (U). Platinum, platinum-13% rhodium thermocouples were used to measure the temperatures of the high temperature furnace (N) and the iodine pentoxide heater (V) at 1120° ± 2° C and 120° ± 1° C respectively. The furnace at 900° ± 10° C and the palladium thimble heater at 350° ± 5° C were controlled by means of powerstats.

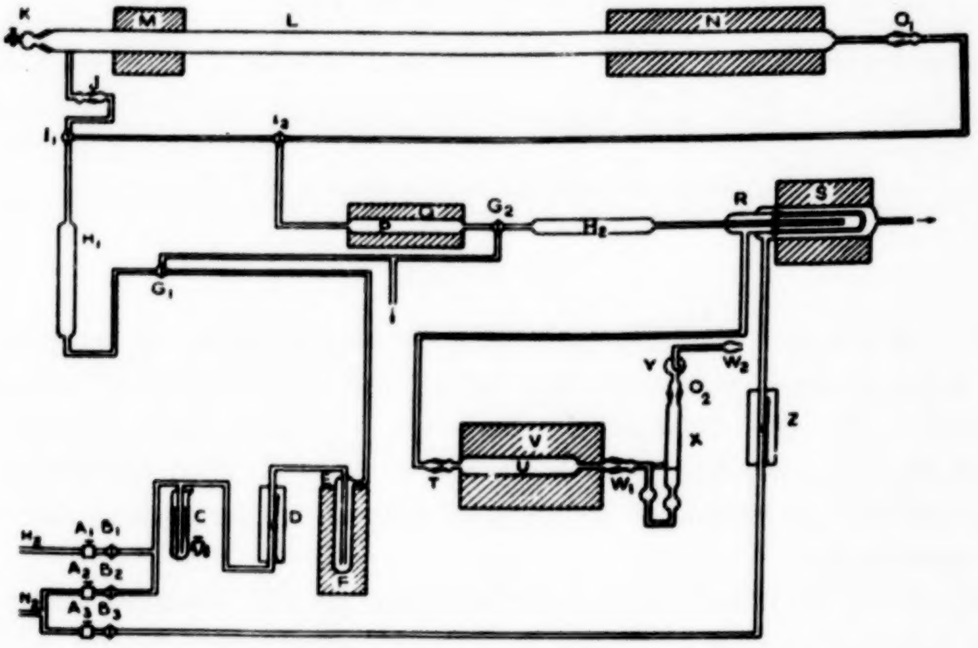

Fig. 1. Unitized direct oxygen apparatus.

A diagram of the apparatus containing the following parts is shown in Fig. 1.

A_1, A_2, A_3.	Needle valves.
B_1, B_2, B_3.	Stopcocks No. 7280.
C.	Overpressure Blowoff, with stopcock No. 7280.
D.	Rotameter No. J-2535-1, catalog J-52, Scientific Glass Apparatus Co. Inc., but with terminals sealed to the glass tube.
E.	Tube with activated copper. The dimensions of the tube are: 30 mm O.D. × 150 mm length.
F.	Heater for activated copper tube (400° to 450° C). No. S-36517, E. H. Sargent Co., Chicago.
G_1, G_2.	Stopcocks No. 7420.
H_1, H_2.	Ascarite-dehydrite tubes. With glass wool plugs (10 mm) at both terminals and packed from the entrance with 100 mm of ascarite, a glass wool plug (10 mm) and 80 mm of dehydrite. The dimensions of the tube are: 11 mm O.D. × 230 mm length.
I_1, I_2.	Stopcocks No. 7450.
J.	Standard taper joint.
K.	Cap for the carbon-reduction quartz tube, with stopcock and standard joint No. 14/35, No. 3882-B4, A. H. Thomas Co. catalog (1950).
L.	Carbon-reduction quartz tube. No. 3882-B3, A. H. Thomas Co. catalog (1950). From the portion of the tube attached to the capillary tube, it is packed with: quartz wool plug (10 mm) and quartz wool plug (10 mm); standard joints are graded sealed to the glass.
M.	Traveling furnace (900° to 1000° C). Dimensions are: 50 mm length and 18 mm hole. It is connected to an electric motor with three constant speeds: 9 mm/min, 22 mm/-min and 33 mm/min.
N.	High temperature furnace (1120° ± 2° C). Constructed according to KIRSTEN[4] but using Jelliff Alloy K. Wire. The proper temperature is maintained by means of an electric control as is shown in Fig. 2.
O_1, O_2.	Standard joint No. 10/30.

P. Copper-gauze quartz tube. Dimensions are: 11 mm O.D. × 230 mm length. Terminals were graded sealed to glass. Constructed using No. 3883-A8 quartz tube, A. H. Thomas Co., catalog (1950).

Q. Furnace (900° ± 10° C). A conventional furnace. Dimensions are: 18 mm I.D. × 230 mm length. The temperature is controlled by means of a powerstat.

R. Palladium thimble. Constructed according to CAMPANILE *et al.*[1].

S. Palladium thimble heater (350° ± 5° C). The temperature is controlled by means of a powerstat.

T. Standard joint No. 12/30.

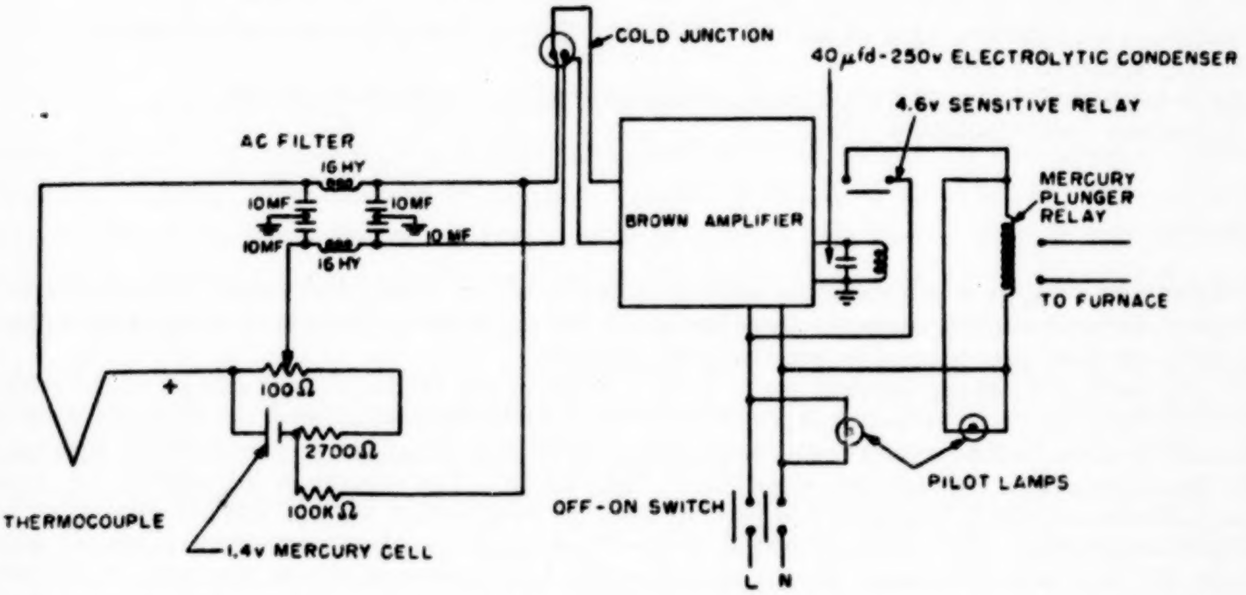

Fig. 2. Circuit used for electronic control of temperature of high temperature furnace and iodine pentoxide heater.

U. Iodine pentoxide tube. Packed from the exit with glass wool plug (10 mm) iodic acid (220 mm) and glass wool plug (10 mm). Dimensions of the tube are: 11 mm O.D. × 270 mm length.

V. Iodine pentoxide heater (120° ± 1° C). Constructed using aluminum tube and Jelliff Alloy K. wire. The aluminum tube is placed between two pieces of insulation material, and the whole enclosed in a suitable metallic case. Dimensions are: 18 mm hole × 230 mm length. The proper temperature is maintained by means of an electronic control as shown in Fig. 2.

W_1, W_2 Standard joint No. 5/20.

X. Absorption-bubbling tube. Sintered glass, 12 mm O.D. × 150 mm length, with three identations at 110 mm from the bottom to break bubbles, two glass bulbs, as shown (15 mm O.D.), and a glass tube 3 mm O.D. between them making connections to the iodine pentoxide tube.

Y. Security bulb 18 mm O.D.

Z. Rotameter No. J-2535, Catalog J-52, Scientific Glass Apparatus Co., Inc. with both terminals sealed to glass tube.

Reagents and materials

The following reagents and materials were used:

Carbon, Wyex Compact Black, F. H. Huber, Inc., available through A. H. Thomas Co., pelletized. The fraction 20 to 50 mesh was used in the carbon-reduction quartz tube (L). It is prepared according to STEYERMARK[10].

Ascarite (sodium hydroxide on asbestos). The commercially available material 8 to 20 mesh from A. H. Thomas Co. It is used in the ascarite dehydrite tubes (H_1, H_2).

Dehydrite. The fraction retained in a 20-mesh screen is used in the ascarite-dehydrite tubes (H_1, H_2).

Iodic acid C.P. This material was sized through a 100-mesh screen and the coarser fraction was used. The iodine pentoxide (probably not iodine pentoxide but anhydro-iodic acid[14] is obtained), used for the oxidation of carbon monoxide is prepared by heating iodic acid in situ at 180° for 24 hours, passing at the same time 30 ml/min of purified nitrogen through the apparatus until a satisfactory and reproducible blank is obtained. Sometimes a further heating at 190° C for several hours is necessary. This reagent may be prepared also according to UNTERZAUCHER[14].

Copper. Wire form prepared from A.C.S. grade cupric oxide by reduction with hydrogen *in situ*. Before reduction the cupric oxide is treated as recommended by UNTERZAUCHER[14].

Copper C.P. 40-mesh gauze.

Quartz wool from A. H. Thomas Co.

Glass wool. Pyrex brand glass No. 722, Corning catalog No. 800.

Nitrogen. High purity, dry (less than 0.01% oxygen content), from Linde Air Products Co.

Hydrogen. Electrolytic commercial grade from Linde Air Products Co.

Potassium acetate-acetic acid solution. Potassium acetate A.R. 25 g dissolved in acetic acid, C.P. at 60° C and diluted to 250 ml.

Sulfuric acid solution. 25 g of sulfuric acid C.P. diluted with 100 g of distilled water.

Iodine solution $0.01N$.

Sodium thiosulphate solution $0.01N$, containing 1% of potassium iodide.

Potassium iodide solution 1%.

Procedure

Before analysing it is advisable to reach a constant blank with a low value (less than 0.02 ml of $0.01N$ solution corresponding to less than 0.008 mg of oxygen). The blank is performed following the complete procedure but omitting the sample.

A solid sample weighing between 3 and 7 mg is weighed in a platinum boat using a microbalance. To obtain reverse flow, stopcock (I_1) is turned to communicate with stopcock (I_2) and from (I_2) the flow is sent to the carbon-reduction quartz tube (L). From here the flow is discharged into the atmosphere through the stopcock in the cap (K). The sample is introduced by means of a platinum hook in a long glass rod placing the platinum boat at about 6 cm in front of the high temperature furnace (N). After 15 min of reverse flow using 30 ml/min of nitrogen the stopcock of cap (K) is closed. The same flow is now directed from stopcock (I_1) to the carbon-reduction quartz tube (L); from stopcock (I_2) the flow is sent to the copper-gauze tube (P) and from this to the ascarite-dehydrite tube (H_2) by means of stopcock (G_2). The traveling furnace (M) is placed near the inlet of carbon-reduction quartz tube (L) and it is turned on. After 15 min the nitrogen flow is reduced to 10 ml/min. The nitrogen flow through the palladium thimble is maintained always at 180 to 200 ml/min. The absorption tube (X) with 10 ml of $0.01N$ sodium thiosulphate solution containing 1% of potassium iodide is put in place carefully and the electric motor of the traveling furnace (M) is turned on using the low speed 9 mm/min.

When the traveling furnace has touched the high temperature furnace (N), the electric motor is turned off and the traveling furnace is left at this place for 5 min. About 10 min before completion of the analysis the standard joint (W_1) and the glass bulb of the absorption tube (X) near to the iodine pentoxide tube are heated slightly with a microburner to recover all the iodine that may be condensed on the walls. After 30 min more the absorption tube (X) is detached from the apparatus and it is rinsed using vacuum, with 90 ml of freshly prepared 1% potassium iodide solution passing the total volume to a 250 ml beaker. Then 1 ml of the potassium acetate-acetic

TABLE I

OXYGEN ANALYSIS OF PURE COMPOUNDS

Sample	*Oxygen wt %*	
	Theory	*Found*
Benzoic acid (National Bureau of Standards)	26.20	26.24
		26.12
		26.30
		26.26
		26.15
		26.19
2- Iodobenzoic acid (National Bureau of Standards)	12.90	12.96
		12.81
2-Chlorobenzoic acid (National Bureau of Standards)	20.45	20.54
		20.50
Cystine (National Bureau of Standards)	26.65	26.64
		26.69

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acid solution and 0.3 ml for the sulfuric acid solution (1:4) are added. The amperometric titration is conducted immediately in the usual manner with the standard 0.01 *N* iodine solution, using a microburette.

Sodium thiosulphate solution 0.01 *N* containing 1% of potassium iodide is prepared daily by dilution of 0.1 *N* sodium thiosulphate standard solution and addition of the proper quantity of potassium iodide.

The copper of the tube (E) and the quartz tube (P) may be reactivated whenever necessary by means of a hydrogen current using the stopcocks (G_1, I_1, I_2 and G_3).

Typical analysis gave the results as shown in Table I.

DISCUSSION

It has been noted that if the cap (K) of the carbon-reduction quartz tube is not opened for 9 to 12 hours and the nitrogen flow is maintained all the time at about 10 ml/min through the carbon-reduction quartz tube and at 180 to 200 ml/min through the palladium thimble, the blank is practically zero. But if the cap (K) is opened to place an empty platinum boat inside the carbon-reduction quartz tube and the reverse flow is maintained for 15 min at 30 ml/min the blank obtained is approximately 0.02 ml of 0.01 *N* solution corresponding to 0.008 mg of oxygen. The conclusion obtained is in accordance with CAMPANILE *et al.*[1], that under the conditions of test the incomplete removal of air by reverse flow operation is the cause of blank.

The oxygen determinations obtained in some pure compounds are shown in Table I; accuracy and reproducibility are within 0.10% oxygen and average about 0.06%.

It would be possible for special purposes to obtain greater sensitivity using prolonged reverse flow operations and more diluted thiosulphate-iodide and iodine solutions. The amperometric titration *in situ* would be also of advantage.

ACKNOWLEDGEMENT

The contribution of Mr. C. I. GLASSBROOK and Mr. LEONARD CAVANAGH in helping to design and build the instrument is acknowledged. This work was done in the laboratory of and with the aid of funds supplied by Stanford Research Institute, Stanford, Calif. Permission to engage in this work was granted to the authors by Stanford Research Institute and Instituto Tecnológico y de Estudios Superiores de Monterrey, N. L. Mexico.

SUMMARY

Quantitative liberation of iodine in the reaction between carbon monoxide and iodine pentoxide used in the SCHÜTZE-UNTERZAUCHER method, is affected by hydrogen and sulfur compounds formed during the pyrolysis of the sample. By appropriate means both causes of error are eliminated.

The absorption of iodine in sodium hydroxide solution, the subsequent multiplication process for iodine of VIEBÖCH AND BRECHER and the titration using the classical starch indicator end-point, are substituted by fixation of iodine in thiosulphate-iodide solution and amperometric titration of thiosulphate in excess.

Increased sensitivity in the final titration is obtained and the multiplication process for iodine is not used, which simplifies the method and saves time.

RÉSUMÉ

La libération quantitative de l'iode lors de la réaction entre l'oxyde de carbone et le pentoxyde d'iode (méthode de SCHÜTZE-UNTERZAUCHER) est gênée par l'hydrogène et les composés sulfurés formés au cours de la pyrolyse de l'échantillon. Il est possible d'éviter ces deux causes d'erreur.

L'absorption de l'iode dans une solution d'hydroxyde de sodium, puis le procédé de multiplication pour l'iode, de VIEBÖCH ET BRECHER, et la titration en présence d'amidon comme indicateur sont alors remplacés par la fixation de l'iode dans une solution de thiosulfate-iodure et par le titrage ampérométrique du thiosulfate en excès.

Une plus grande sensibilité est obtenue dans le titrage final et de plus, le procédé de multiplication pour l'iode est supprimé, ce qui simplifie la méthode et permet de gagner du temps.

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ZUSAMMENFASSUNG

Die quantitative Bestimmung des Jods, durch Einwirkung des CO auf J_2O_5 in der SCHÜTZE-UNTERZAUCHER Methode, wird durch die pyrolytische Entwicklung von Wasserstoff und Schwefelverbindungen gestört. Man kann aber die beiden Fehlerquellen eliminieren.

Die Absorption des Jods in NaOH, die Jod-Multiplikationsmethode von VIEBÖCH UND BRECHER und die klassische Titration mit Stärke werden durch Jod-Fixierung in Thiosulphat-Jodid-Lösung und durch eine amperometrische Titration des überschüssigen Thiosulphats ersetzt. Eine grössere Empfindlichkeit in der letzten Titration wird erreicht, die Multiplikationsmethode für Jod wird nicht benützt und der Arbeitsgang ist damit vereinfacht.

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DETERMINATION OF SMALL QUANTITIES OF HYDROGEN IN THE INERT GASES

by

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INTRODUCTION

High temperature atomic reactor systems require inert gas blankets which are low in gaseous contaminants that have corrosive effects when in contact with metal-liquid metal systems. Such contaminants are hydrogen and oxygen. A precise analytical method has been developed to show that the oxygen content in tank helium can be reduced from a concentration of 5 to 20 p.p.m. to less than 0.5 p.p.m. by bubbling the helium through cold NaK[1,2].

No rapid procedure for the determination of hydrogen (0 to 10 ppm) has been written which could be used to ascertain the best method for removal of hydrogen from inert gases.

The determination of small amounts of hydrogen in helium by physical methods such as thermal conductivity is difficult because of the similarities in physical properties of the two gases. Consequently, the investigation of colorimetric methods was undertaken, using reagents which are sensitive to activated hydrogen. Three such reagents were studied. They are anthraquinone di-sulfonates investigated by BONNEY AND HUFF[3] for their hydrogen absorption properties; sodium molybdate solution used by MACPHEE[4] to determine olefinic hydrocarbons in air; and methylene blue solution used by PESEZ[5] as a qualitative test for large concentrations of hydrogen. All of these reagents require a palladium catalyst to activate the hydrogen.

After preliminary tests, the methylene blue-palladous chloride solution was selected as the reagent for molecular hydrogen. According to PESEZ[5] the palladous chloride is reduced by the hydrogen to metallic palladium. This reaction catalyzes the reduction of methylene blue to a leuco-derivative. Conversely, the leuco-methylene blue is oxidized to its normal colored form by atmospheric oxygen. A solution of concentrated methylene blue-palladous chloride can be put through several reduction-oxidation cycles before it is exhausted.

REAGENTS

Methylene blue, stock solution — Dissolve 10 mg of methylene blue in 100 ml of water.

Palladous chloride solution — Dissolve 1 g of $PdCl_2$ in 1250 ml water.

Methylene blue — $PdCl_2$ reagent — Pipette 25 ml of stock methylene blue solution and 5 ml of $PdCl_2$ solution into a 200 ml volumetric and dilute to volume with distilled water.

Sodium-anthraquinone-β-sulfonate, Brady reagent[6] — Dissolve 0.0313 g sodium-anthraquinone-β-sulfonate in 300 ml of hot distilled water.

Add 10 ml of sodium hydroxide. Cool and dilute to 500 ml.

Sodium-anthraquinone-β-sulfonate — $PdCl_2$ solution — Pipette 1 ml $PdCl_2$ solution into a 25 ml volumetric and dilute to volume with Brady reagent.

Palladous sulfate solution — C.p., 10% aqueous solution, purchased from Fairmount Chemical Co., Newark, N. J.

Sodium molybdate reagent[4] — Dissolve 6.1 g sodium molybdate in 25 ml H_2O, add 0.35 ml palladous sulfate solution, 40 ml glacial acetic acid, and 40 ml H_2SO_4.

Sulfuric acid solution — Add 22 ml of concentrated sulfuric acid to 180 ml of water.

Sodium anthraquinone-β-sulfonate, scrubbing solution[6] — Dissolve 0.75 g of sodium anthraquinone-β-sulfonate in 490 ml of distilled water and make up to 500 ml with 30% NaOH solution.

Amalgamated zinc — 20 mesh — Stir 400 g of granulated zinc with 400 ml of 5% mercuric chloride solution for ten minutes. Drain off the mercuric chloride solution and wash thoroughly with distilled water.

APPARATUS

In principle the apparatus is similar to that used by BRADY[6], for determining oxygen in helium. The sample gas circulates a given amount of liquid reagent through an optical absorption cell. In the process, the gas constituent under analysis (oxygen) manifests a color change which is measured photometrically. This apparatus was modified further by SILVERMAN AND BRADSHAW[2] to obtain more efficient oxygen absorption, permitting the spectrophotometric determination of very low concentrations of oxygen in helium. The principles used in the modified Brady apparatus were extended to construct an apparatus specific for the determination of hydrogen in helium.

Analytical system

The analytical system for hydrogen is shown in Figs. 1 and 1a. The test gas is passed through an oxygen absorption bulb A, into the gas scrubber B, mixing with the analytical solution at the liquid-gas contact point. The gas separates from the liquid in the liquid-gas separator C, passes on through a liquid waste trap D and is measured quantitatively in a wet test meter.

The methylene blue solution, reagent grade, is stored in a reagent bottle E and is partially reduced by tank hydrogen just prior to use. Stopcock F controls the liquid level and its direction of flow. The absorption cell G permits the spectrophotometric measurement of the absorbance of the analytical solution, by a Beckman model DU spectrophotometer. The purpose of the section of 2 mm capillary H is to retard and prevent back-flow of the sample gas.

Critical measurements are included in the sketch. The diameter of glass tubing connections is 8 mm, except in the gas-scrubber. Here a 4-mm tube is fused into the inner bore of the scrubber;

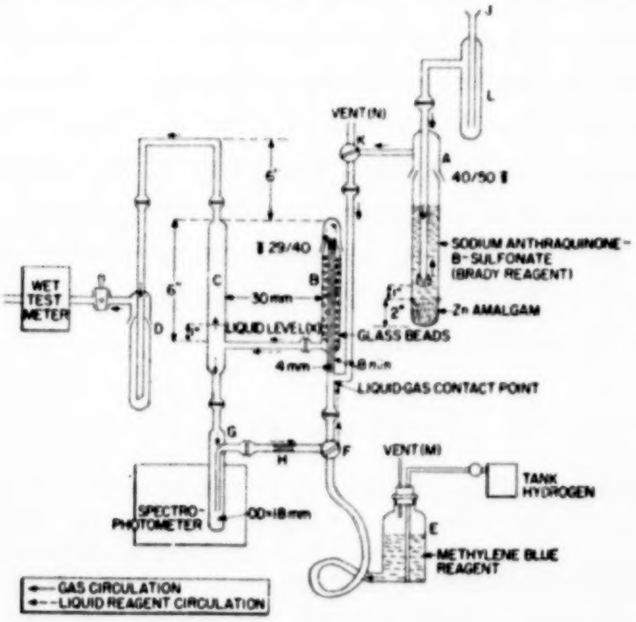
J
L
VENT (N)
K
A
40/50
SODIUM ANTHRAQUINONE-B-SULFONATE (BRADY REAGENT)
1"
2"
Zn AMALGAM
6"
29/40
B
C
6"
30mm
D
1/2"
LIQUID LEVEL (X)
GLASS BEADS
4mm
8 mm
LIQUID GAS CONTACT POINT
WET TEST METER
G
H
F
VENT (M)
TANK HYDROGEN
E
METHYLENE BLUE REAGENT
SPECTRO-PHOTOMETER
OD=18mm
GAS CIRCULATION
LIQUID REAGENT CIRCULATION

Fig. 1. Analytical system for hydrogen determination.

this facilitates the pumping action of the gas pressure. The diameter of the liquid-gas separator should be the same bore as the outside bore of the scrubber so that the gas pressure does not draw an excess of liquid into the waste trap D. The liquid level (X) should be kept constant at about one inch above the side arm of the liquid-gas separator. The top of the gas-separator C should be level with the top of the liquid-gas scrubber B.

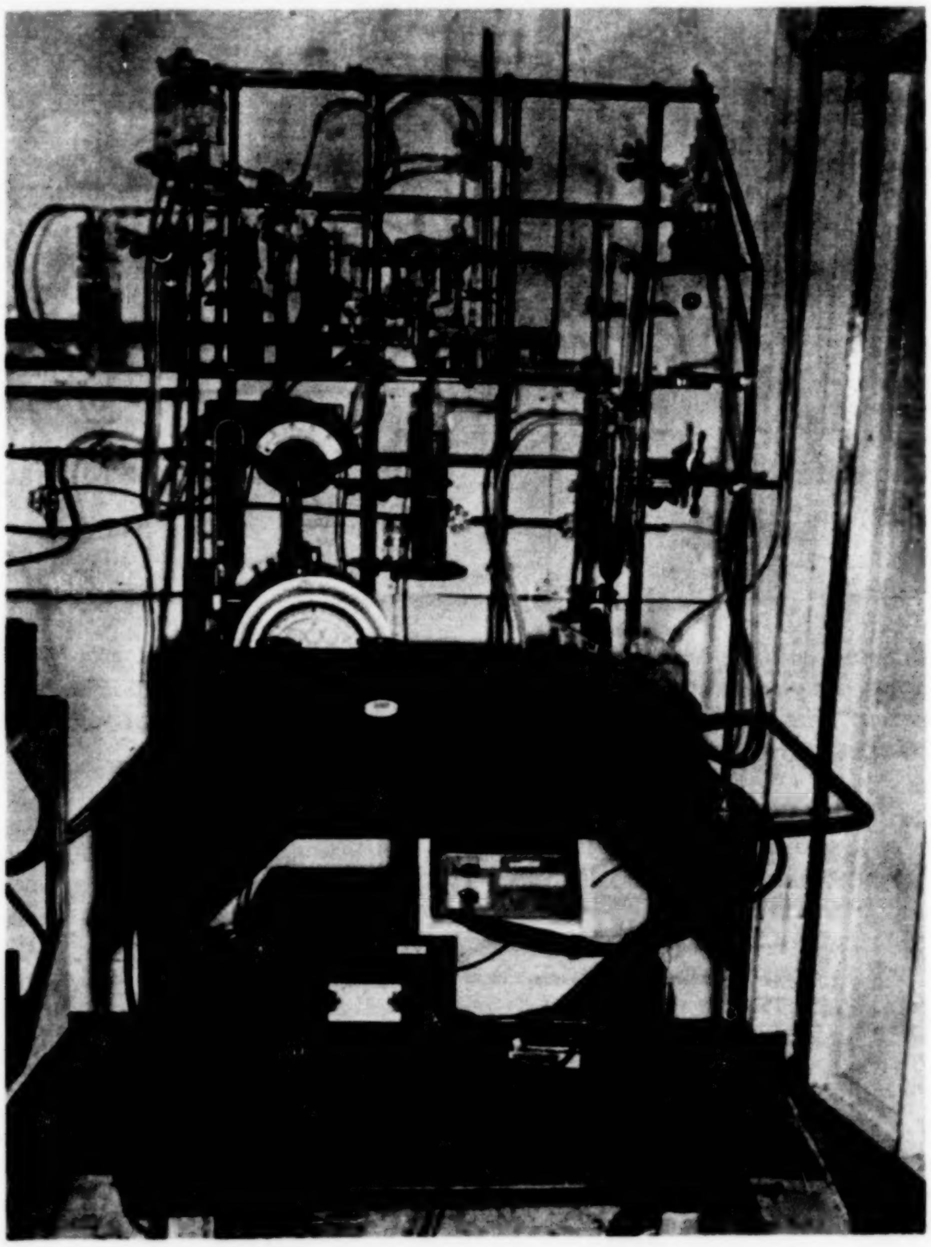

Fig. 1a.

Calibration systems

Two types of calibration systems were used. They were connected to the analytical system by ball and socket joint at the point J.

In preliminary runs hydrogen generated from zinc was attempted for calibration of the system. The calibration vessel (Fig. 2) contained a weighed amount of zinc to which a dilute solution of hydrochloric acid was added. The hydrogen liberated was swept along by a purge of de-oxygenated helium gas.

In the electrolytic calibration vessel (Fig. 3) hydrogen generated from sulfuric acid at the cathode is separated by distance and spaced by two fritted discs from oxygen generated at the anode. The hydrogen is swept into the analytical system by de-oxygenated helium, while the oxygen is swept from the surface of the liquid by tank helium. The vessel is completely reversible so that the electrodes can be reversed.

The electrodes are 20-mil platinum wire. A milliammeter current is supplied through a rectifying control unit. The current can be read by a 0-25 milliammeter, accurate to one per cent.

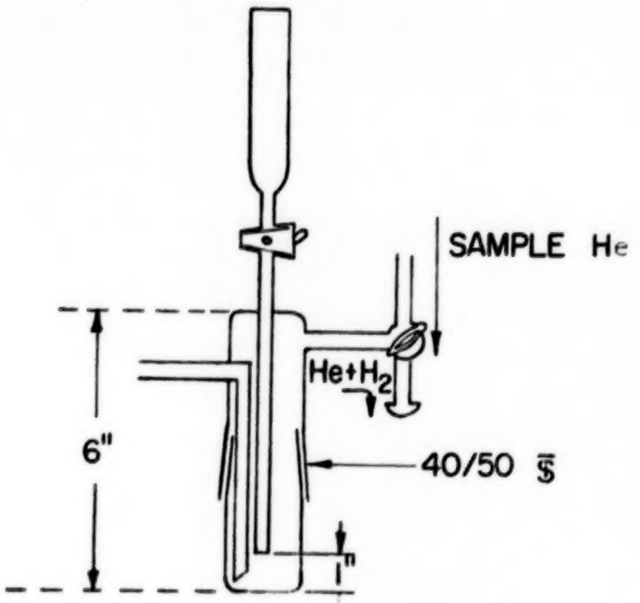
SAMPLE He
He+H₂
6"
40/50 $
1"

Fig. 2.
Zinc-hydrochloric acid calibration vessel.

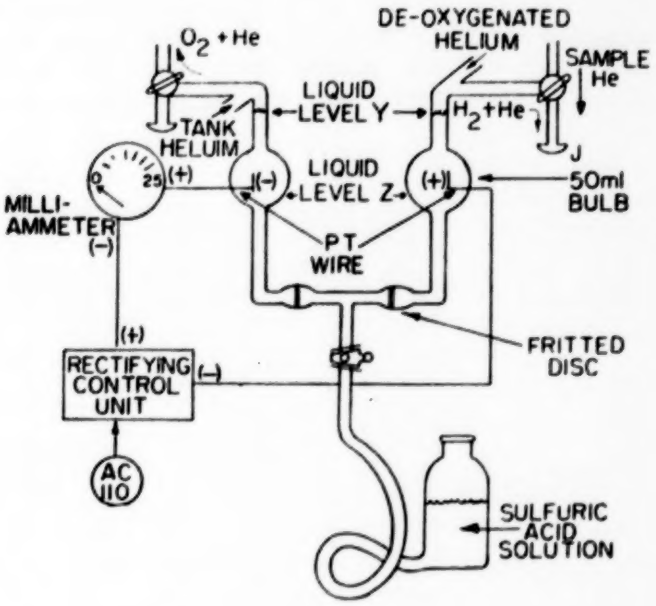
O₂ + He
DE-OXYGENATED HELIUM
SAMPLE He
TANK HELUIM
LIQUID LEVEL Y
H₂+He
J
MILLI-AMMETER
0
25
(+)
(−)
LIQUID LEVEL Z
(+)
(−)
50ml BULB
PT WIRE
FRITTED DISC
RECTIFYING CONTROL UNIT
(+)
(−)
AC 110
SULFURIC ACID SOLUTION

Fig. 3.
Electrolytic calibration vessel.

Gas-handling system

Because methylene blue is sensitive to molecular oxygen, a special gas-handling system is necessary to supply oxygen-free gas for calibration and analytical purposes. A schematic of the gas flow is shown in Fig. 4. Helium, or other sample gas, is passed through a drierite tube to either of two oxygen absorber trains.

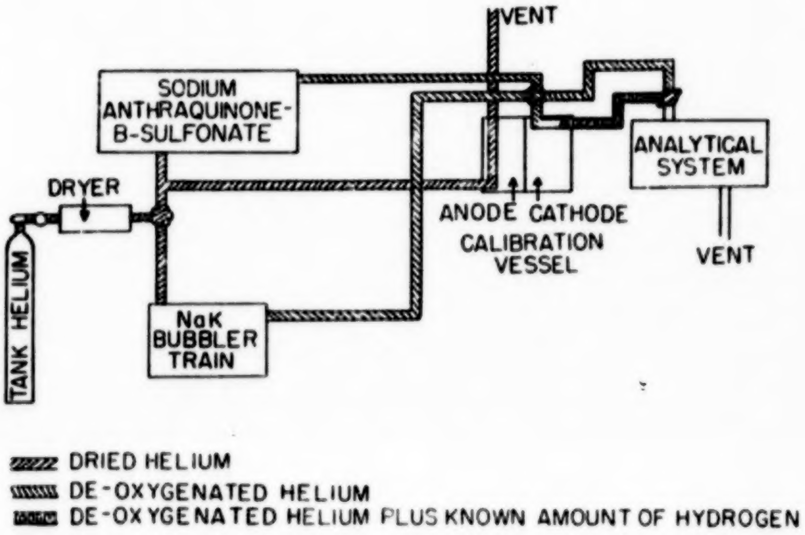
VENT
SODIUM ANTHRAQUINONE-B-SULFONATE
DRYER
ANALYTICAL SYSTEM
ANODE CATHODE
CALIBRATION VESSEL
VENT
NaK BUBBLER TRAIN
TANK HELIUM
▨ DRIED HELIUM
▨ DE-OXYGENATED HELIUM
▨ DE-OXYGENATED HELIUM PLUS KNOWN AMOUNT OF HYDROGEN

Fig. 4. Gas-handling system.

A NaK bubbler train containing at least 500 ml of sodium-potassium alloy is capable of reducing the oxygen concentration of helium, argon, or dry nitrogen to less than 0.5 p.p.m.[1]. Since we planned to study the hydrogen concentration of helium before and after passage through a NaK bubbler, a different type of de-oxygenator was also necessary.

The alternate train consisted of three gas scrubbing bottles, each containing 150 ml of sodium anthraquinone-β-sulfonate, scrubbing solution, plus 133 g of amalgamated zinc shot. The zinc shot was prepared in the same manner as the granulated zinc. Such a train can reduce the oxygen concentration of tank helium or argon to less than 0.5 p.p.m. oxygen but cannot be used with dry nitrogen which contains 2000 or more p.p.m. oxygen[2,7].

The de-oxygenated helium is passed over the cathode of the calibration cell during calibration, or directly to the analytical system for analysis. During a calibration run, tank helium is passed over the anode in order to equalize pressures and to sweep away the liberated oxygen.

PROCEDURE FOR THE DETERMINATION OF HYDROGEN IN INERT GASES

Assemble the analytical system as shown in Fig. 1. Purge it of air with de-oxygenated gas. During this time prepare 200 ml of methylene blue-$PdCl_2$ reagent and place it in the reagent bottle E. With stop-cock F in closed position, and vent (M) open, purge the reagent with tank hydrogen until the solution turns almost colorless. Shut off the hydrogen purge, close vent (M), vent the sample gas through stop-cock K and vent (N), open stop-cock F to the reagent bottle and fill the system with the *partially* reduced solution. Bring the reagent to the proper liquid level (X), draining excess reagent into the reagent bottle under positive gas pressure by reopening stop-cock K to the sample gas. Repeat these steps 2 to 3 times until the liquid is homogeneous.

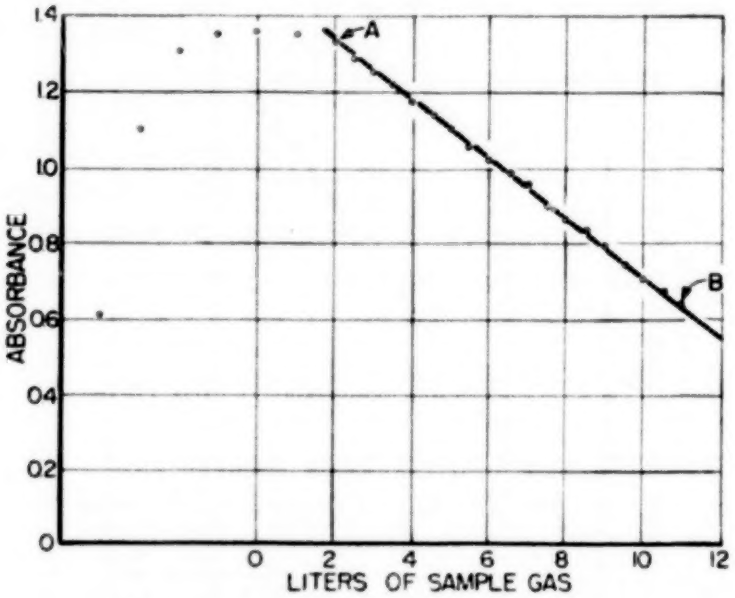

Fig. 5. Typical hydrogen analysis.

Then, with stop-cock K open to the sample gas regulate the gas flow to approximately 0.5 liter per minute. As the gas circulates through the reagent traces of residual oxygen in the system will darken the color again (residual oxygen being absorbed). Check the absorbance of the solution at 655 mμ and slit width of 0.15 while the gas is flowing. When a plot of absorbance *versus* volume of gas (Fig. 5) levels off and then begins to decrease, the hydrogen analysis has begun.

[Should the absorbance level off at a value greater than 1.45 (due to oxygen pick-up), discontinue and start the analysis over because the reagent has maximum and reproducible sensitivity to hydrogen (in our system) only when its absorbance ranges from 1.45 to 0.0.]

To complete the analysis, continue spectrophotometer readings at regular intervals, and record the absorbance and volume of gas. If the hydrogen concentration is less than one part per million, continue the analysis until 10 to 20 liters of gas have been monitored and the plotted points form a straight line. If the hydrogen concentration is greater than 1 part per million, continue the analysis until 5 to 10 liters of gas have been monitored and the plotted points form a straight line.

Calculate the hydrogen concentration of the gas from the corrected analytical plot and the calibration factor.

$$\text{Analytical tangent (absorbance per liter)} = \frac{\triangle A}{\triangle V} \qquad (1)$$

Where $\triangle A$ = the change in absorbance observed between points A and B,

$\triangle V$ = the difference in gas volume, in liters, between points A and B, corrected to standard conditions.

Refer to a calibration curve (Fig. 6) and read the hydrogen concentration in parts per million.

To make another run, re-oxidize the solution by exposing it to air. Carry out the analysis as before. Since the methylene blue-$PdCl_2$ is not inexhaustible, make up fresh methylene blue-$PdCl_2$ reagent each day.

PREPARATION OF THE CALIBRATION CURVE

Connect the calibration vessel (Fig. 3) to the assembled analytical system at the point J. Bring the level of the sulfuric acid to level Z, and connect the de-oxygenated helium so it flows through part of the calibration vessel as illustrated in Fig. 3. Purge the system with de-oxygenated helium.

Prepare the methylene blue reagent as if for analysis. Reduce it partially, adjust the liquid level to level X (Fig. 1) and the flow-rate to about 0.5 liter per minute, and then take absorbance measurements.

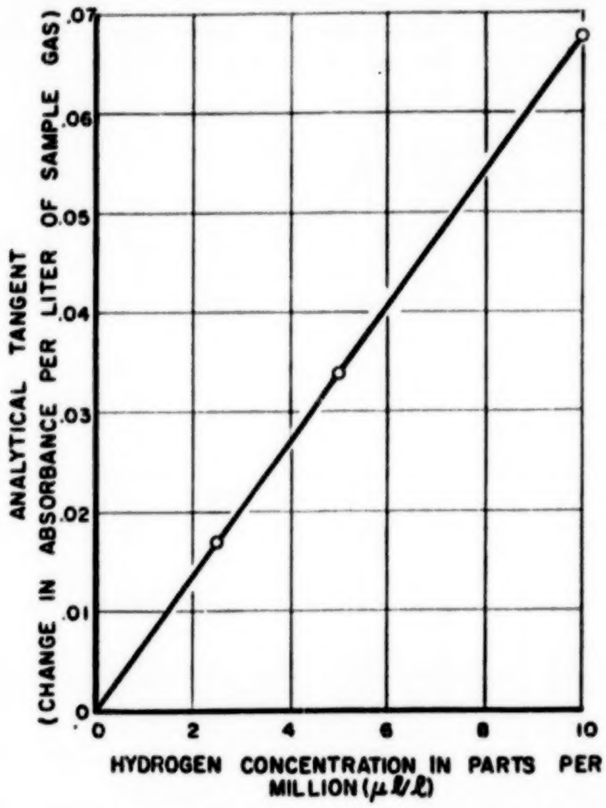

Fig. 6. Calibration curve — analytical tangent versus hydrogen concentration.

Monitor from 5 to 10 liters of gas in order to establish the hydrogen blank of the helium gas. Raise the sulfuric acid level to level Y and balance the pressure of tank helium and de-oxygenated helium so that the liquid level remains constant.

Switch in the rectifying control unit, adjust the current to three milliamperes, start a stop-watch, and read the absorbance. Record absorbance at exactly one or

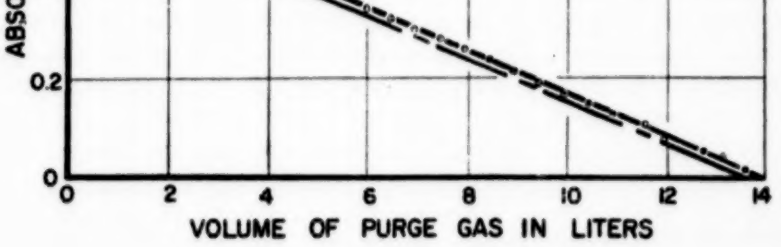

Fig. 7. Typical calibration plots.

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two minute intervals and record the volume of carrier gas at the same time. Maintain the current flow at exactly three milliamperes. Continue readings until the absorbance has decreased about 0.500.

Prepare calibration plots as follows. Plot the hydrogen blank of the helium purging gas (Fig. 7). Calculate the corrected absorbance by subtracting the blank plot from the calibration plot observed during the calibration run (Fig. 7). Calculate the amount of hydrogen generated over the time interval of the calibration run from the following equation:

$$\text{Hydrogen (in microliters)} = 0.0323\ I\,t\,\frac{T}{P} \qquad (2)$$

Where I = the current in milliamperes,
t = the time in seconds,
T = room temperature, °K,
P = the barometric pressure in millimeters.

Calculate the calibration factor F (absorbance change per microliter hydrogen) as follows:

$$F = \frac{A^1}{V^1} \qquad (3)$$

Where A^1 = change in corrected absorbance for a given volume of hydrogen,
V^1 = the volume of hydrogen in microliters, as calculated by equation 2.

Set up the calibration curve (Fig. 6) by plotting hydrogen in parts per million as abscissa against the "analytical tangent" as ordinate. This ordinate is obtained from the calibration factor F (as shown in Eq. 3 above) as follows:

$$\text{"analytical tangent"} = F \times \text{Hydrogen in p.p.m.} \qquad (4)$$

Make a series of calibration runs and calculate the average calibration factor.

EXPERIMENTAL

Selection of a colorimetric reagent

The absorptive properties of the three solutions in question were investigated by quantitatively generating hydrogen from zinc. A closed system was used, but it was not purged of air by helium. The methylene blue solution was the most sensitive to hydrogen (Table I), *i.e.* a given amount of hydrogen effected the greatest color change.

The methylene blue solution is 70 times as sensitive to hydrogen as the sodium molybdate reagent and 4 times as sensitive as the anthraquinone reagent. The sensitivity of the first two solutions is improved in an inert atmosphere, because they are both sensitive to oxygen. Oxygen reverses the color change effected by the hydrogen. The sodium molybdate reagent is not sensitive to oxygen but it is sensitive to olefinic contaminants in the air which also have a reducing effect.

On the basis of its superior sensitivity methylene blue was selected.

TABLE I

ABSORPTION OF HYDROGEN BY VARIOUS REAGENTS (10 ml)

Reagent	*Color change*	*Absorbance read at*	*Change in absorbance, effected by one ml hydrogen*
Methylene blue — $PdCl_2$	Blue to colorless	655 mμ	>0.735
Sodium-anthraquinone-β-Sulfonate — $PdCl_2$	Colorless to red	495 mμ	0.04
Sodium-molybdate — $PdSO_4$	Yellow to blue	675 mμ	0.01

Factors affecting methylene blue sensitivity

1. *Absorbance and methylene blue concentration*

Absorbance curves (Fig. 8) of methylene blue solutions show that the wavelength of maximum absorbance occurs at 655 millimicrons. The effect of varying methylene blue concentrations is also noted in Fig. 8. The solution approaches maximum absorbance as the methylene blue concentration increases from 8 to 16 ml stock solution per 100 ml volume. An intermediate concentration of 12.5 ml of stock solution per 100 ml volume was chosen for the final work.

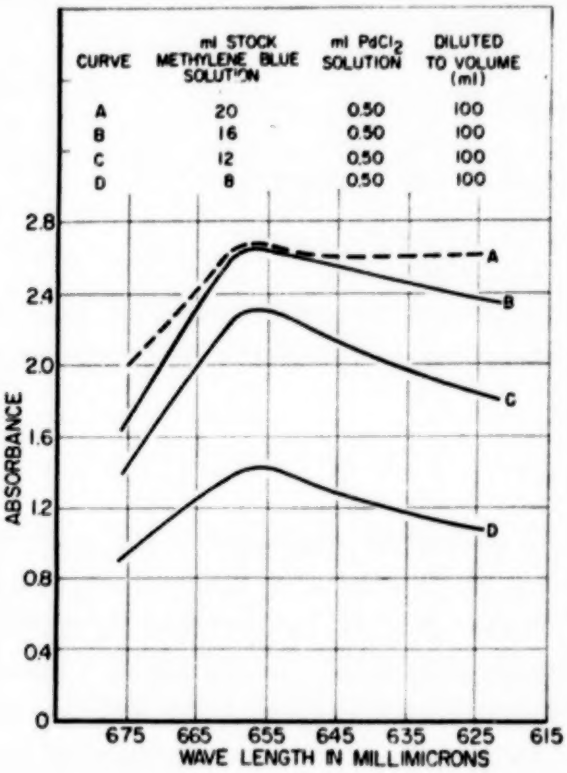

Fig. 8. Effect of methylene blue concentration on absorbance.

2. *Concentration of $PdCl_2$, and life of solution*

The concentration of $PdCl_2$ used is of the order of that recommended by PESEZ[4]. Doubling the concentration of $PdCl_2$ did not affect the sensitivity of the solution.

When the methylene blue-$PdCl_2$ solution is put through repeated reduction-oxidation cycling there is a decrease in the efficiency of the solution, which can be partially alleviated by the addition of more $PdCl_2$. However, the most reproducible results are obtained by preparing a fresh methylene blue-$PdCl_2$ solution each day.

3. *Effect of pH (acid, alkaline and ammoniacal contaminants)*

Methylene blue reagent was mixed with varying amounts of hydrochloric acid, potassium hydroxide and ammonium hydroxide and allowed to stand for a period of 2 to 4 days in order to test the effect of pH on the absorbance and sensitivity of the reagent.

The methylene blue reagent has a pH of 3.8 to 4.0 when prepared as specified. A slight decrease in pH to 3.2 causes marked decrease in absorbance (Fig. 9) and in sensitivity to hydrogen. A decrease to pH of 2.2 causes complete decolorization of the solution within two days time.

An increase in pH also causes decrease in absorbance (Fig. 10), a shift in the absorbance maximum, and a decrease in sensitivity to hydrogen. At equal pH, potassium hydroxide has a more deleterious effect than ammonium hydroxide.

The effects observed are not due to pH alone because when both HCl and KOH are present, the decrease in absorbance is greater than it would be if acid only were present (Fig. 9).

The solution when prepared as specified has the proper pH. In normal operation, no acid or alkaline contaminants are introduced into the methylene blue-$PdCl_2$ reagent. However, in calibration, some caution must be taken so that no sulfuric acid (electrolytic solution) is pressurized into the analytical system. This hazard and the possibility of entrained NaK can be eliminated by inserting a liquid trap L (Fig. 1) between the analytical system and the gas inlet from the calibration system.

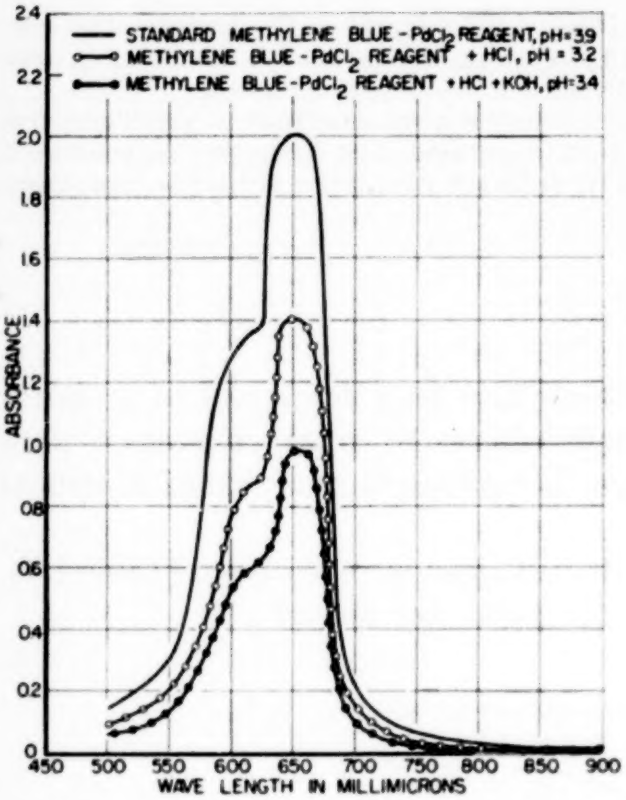

Fig. 9.
Effect of hydrochloric acid and potassium hydroxide in the decreasing pH range.

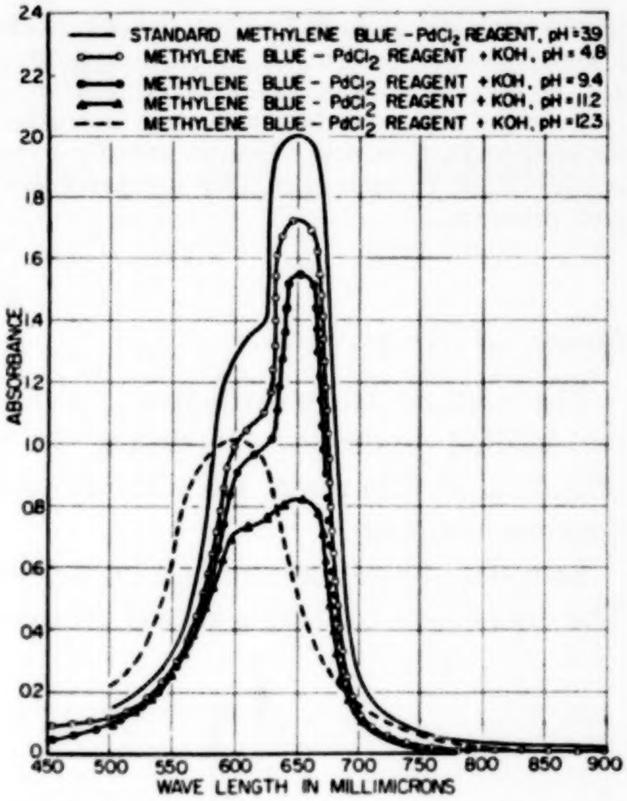

Fig. 10.
Effect of potassium hydroxide in the increasing pH range.

Other factors

The presence or absence of light does not affect the stability of the reagent. Prolonged exposure to air causes a slight fading of the methylene blue-PdCl$_2$ reagent, but this factor is eliminated when the solution is freshly prepared each day.

Calibration

The first attempts at calibration were made using the calibration cell shown in Fig. 2. Hydrogen was slowly liberated by a weighed amount of zinc from a 1:4 solution of hydrochloric acid and the liberated hydrogen was swept into the analytical system by helium. However, the amount of hydrogen liberated by a weighable amount of zinc is too great to be absorbed quantitatively by the methylene blue-PdCl$_2$ solution (Table II).

The results were more quantitative when hydrogen was generated electrolytically from sulfuric acid (Table II). In such calibration the hydrogen generated at the cathode is swept into the analytical system with de-oxygenated helium. Any oxygen which might have diffused back

TABLE II

ABSORPTION OF HYDROGEN BY METHYLENE BLUE-PdCl$_2$ REAGENT

Hydrogen concentration in p.p.m.	*Change in absorption per ml hydrogen*	*Method of production of hydrogen*
9000	0.07	50.2 mg Zn + HCl, Helium sweep
3000	0.09	13.4 mg Zn + HCl, Helium sweep
800	0.15	24.3 mg Zn + HCl, Helium sweep
99	0.3	4.4 mg Zn + HCl, Helium sweep
22.7	3.9	10 mA/sec; He sweep at 0.5 l/min
15.0	4.3	6 mA/sec; He sweep at 0.5 l/min
10.5	6.9	3 mA/sec; He sweep at 0.5 l/min
7.7	6.7	3 mA/sec; He sweep at 0.5 l/min

to the cathode is caught in the oxygen absorber A (Fig. 1). The liquid in the oxygen absorber, a sensitive colorimetric reagent for oxygen[6], indicated that there was no back diffusion of oxygen gas. It follows then, as a corollary, that no back diffusion of hydrogen occurred.

The results obtained for hydrogen absorption are quantitative when a current of 3 milliamperes (or less) and a flow rate of purge gas of 0.5 liters per minute are used. The hydrogen so generated is equivalent to approximately 4.5 parts per million at ordinary conditions of room temperature and pressure.

RESULTS

Range for the procedure

The method is quantitative, *i.e.* follows Beer's law from fractional to 10 parts per million hydrogen, according to the graph calculated from calibration data (Fig. 11). In this range ten microliters hydrogen is equivalent to a change in optical density of 0.067.

Samples of hydrogen in helium, argon, and dry nitrogen were analysed (Table III). The hydrogen contents varied from 0.2 to 6.2 parts per million.

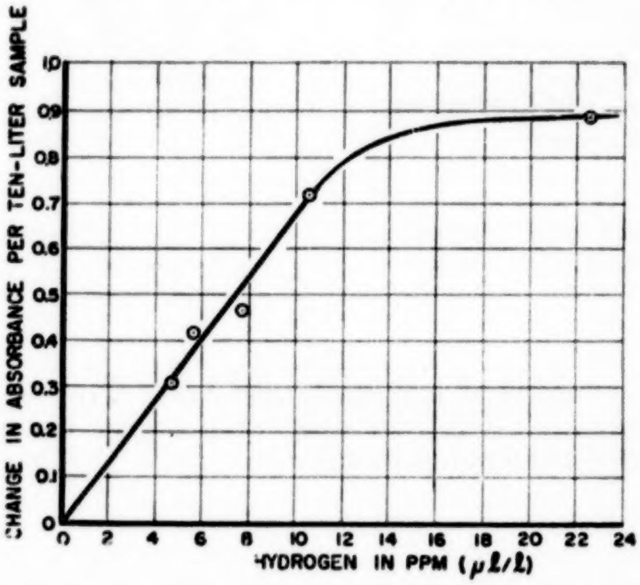

Fig. 11. Quantitative absorption of hydrogen by methylene blue-palladous chloride solution.

Reproducibility

Various samples of helium, argon and nitrogen were analysed for hydrogen content. The standard deviation ranged from 0.1 to 0.2 when the hydrogen content was 0.2 to 6 parts per million (Table III). The analyses are reproducible from day to day.

DISCUSSION

Several colorimetric reagents were investigated for their suitability to the analysis of small amounts of hydrogen in inert gases. Methylene blue $PdCl_2$ reagent was selected as the most sensitive reagent for hydrogen. Since the reaction is reversed by molecular oxygen, a completely oxygen-free carrier gas is necessary. This can be accomplished by the use of a system of NaK bubblers or a system of gas-scrubbers containing sodium anthraquinone-β-sulfonate.

The optimum pH for absorption of hydrogen by methylene blue $PdCl_2$ reagent is 3.9. The reagent can be put through several reduction-oxidation cycles before the

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TABLE III

HYDROGEN ANALYSES OF VARIOUS GAS SAMPLES

Sample gas	*Sample number*	*Hydrogen in p.p.m. (µl/l)*		
		Individual analysis	*Average*	*Standard deviation*
Helium	1	5.5 5.3 5.1	5.3	0.2
	2	4.4 4.1 4.1	4.2	0.2
	3	2.8 2.7 2.4	2.6	0.2
	4	0.3 0.2 0.1	0.2	0.1
Argon	1	6.5 6.5 6.1	6.4	0.2
	2	2.9 2.6 2.6	2.7	0.2
Nitrogen	1	2.2 2.0 1.8	2.0	0.2
	2	1.3 1.1	1.2	0.1

sensitivity to hydrogen is reduced. However, it is best to prepare the reagent fresh daily to avoid exhaustion or poisoning of the $PdCl_2$ catalyst.

The range of the method is 0.1 to 10 parts per million hydrogen using gas samples of 5 to 20 liters in a continuous type of analysis. The precision of the method is ± 0.1 to ± 0.2 parts per million.

SUMMARY

A sensitive reagent, methylene blue-$PdCl_2$ is applicable to the determination of smaller amounts of hydrogen in inert gases. Using this reagent, and a continuous gas-flow type of analysis, the range of the method is 0.1 to 10 parts per million hydrogen with a standard deviation of ± 0.1 to ± 0.2 parts per million. The amount of sample gas needed is 5 to 20 liters. It must be oxygen-free before analysis for hydrogen. This method of hydrogen analysis can be used for inert gas systems consisting of helium, argon, or nitrogen.

RÉSUMÉ

Un réactif sensible, bleu de méthylène-$PdCl_2$, est proposé pour le dosage de faibles quantités d'hydrogène dans les gaz inertes. La méthode décrite permet de doser des teneurs en hydrogène de 0.1 à 10 p.p.m. avec une erreur de ± 0.1 à ± 0.2 p.p.m. La quantité de gaz à analyser nécessaire est de 5 à 20 litres, il doit être exempt d'oxygène. Ce procédé peut être employé pour le dosage de l'hydrogène dans des gaz inertes tels que hélium, argon ou azote.

ZUSAMMENFASSUNG

Ein empfindliches Reagenz Methylenblau-$PdCl_2$ kann zur Bestimmung kleiner Wasserstoffmengen in inerten Gasen dienen. Mit diesem Reagenz kann man, bei Anwendung einer kontinuierlichen Gasstrom-Analyse-Methode, 0.1 bis 10 Teile pro Million Wasserstoff mit einem Fehler von ± 0.1 bis 0.2 Teilen pro Million bestimmen. Die benötigte Gasmenge beträgt 5 bis 20 Liter. Das Gas muss frei von Sauerstoff sein. Das beschriebene Verfahren kann zur Bestimmung von Wasserstoff in inerten Gasen, wie Helium, Argon oder Stickstoff angewendet werden.

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ION DIMENSIONS AND R_F VALUES IN RADIAL PAPER CHROMATOGRAPHY

by

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The purpose of this research was to investigate the existence of a possible relation between the R_F exhibited by inorganic cations and some other properties either of the ions or of the mobile phases used to make them run. From a previous study[1] it appears that, when densitometric areas, D, are plotted against values of the corresponding concentrations, C, the linear relation given by $D = a.C$ (where the value of a corresponds to the inclination of the straight line) is pointed out. Such value being inversely proportional to C, is directly proportional to a volume; since ionic volumes are functions of ionic radii, the dependence of dynamic factors on ionic dimensions, *i.e.*, the relation between R_F values and ionic radii, has been investigated.

Ions of the same sub-group were employed, namely: Zn, Cd, Hg; Li, Na, K, Cs; Be, Mg, Ca, Sr, Ba, using 0.05 ml of the corresponding nitrates (200 γ of cation). The upper layer of *n*-butanol-water-nitric acid mixtures (prepared by shaking *n*-butanol with the same volume of HNO_3 solutions of increasing normality from N to $4N$) has been found to be the most suitable mobile phase as it has previously been successfully used[2,3] and as, containing no complex-forming agent, it requires the smallest number of relations to define the system.

To obtain information about the mobility of the ions, some physical properties of the above-mentioned solutions were measured at 20° C. The experimental data demonstrate clearly the dependence of potential difference (from 400 to 432 mV), density (from 0.853 to 0.945) and surface tension (from 27.62 to 31.75 dyne/cm) on the acid concentration. The relative viscosity (from 0.0388 to 0.0371) shows a maximum (0.0407) at the point corresponding to the $1.5N$ HNO_3-butanol-water solution. Nevertheless, the mobility of the ions is not greatly affected by the viscosity of the mobile phase.

For the R_F determination we followed the principle of adopting a reagent suitable for detecting most of the cations considered; only Zn, Cd, Be, Mg, Ca, Sr, Ba, when observed in u.v. light, give brilliant fluorescent bands with the 8-hydroxyquinoline-kojic acid reagent; Hg is detected with ammonia solution of H_2S, K with sodium cobaltinitrite, Li with potassium periodate, and Na with zinc-uranyl acetate; Zn, Cd and Hg are confirmed with dithizone, Li and K spectroscopically.

From the direct observation of the developed chromatograms, a deepening of the colour towards the outside of the circular crown is evident. This phenomenon, better detectable densitometrically, is responsible for the shape of the area within the curve which is obtained by plotting the displacements in mm against the values of optical density. The resulting triangle is not isosceles as the external edge of the band has a rather strong inclination. As the same phenomenon had been observed when using as mobile phase the complex-forming mixture benzoylacetone-butanol-water-nitric acid[1], it is clear that it is not due to the presence and the nature of the complex-forming agent, but to the anisotropic diffusion along the radius of the chromatogram.

The R_F values, recorded in Table I, show that ions of the same sub-group do not exhibit extremely similar mobility.

TABLE I

HNO_3 Normality	Zn^{+2}	Cd^{+2}	Hg^{+2}	Li^+	Na^+	K^+	Cs^+	Be^{+2}	Mg^{+2}	Ca^{+2}	Sr^{+2}	Ba^{+2}
1.0	0.245	0.269	0.696	0.390	0.210	0.222	0.237	0.225	0.255	0.240	0.176	0.216
1.25	0.262	0.286	0.709	0.398	0.223	0.231	0.245	0.235	0.263	0.249	0.186	0.226
1.5	0.278	0.303	0.723	0.406	0.236	0.241	0.254	0.244	0.271	0.259	0.195	0.237
1.75	0.287	0.313	0.735	0.415	0.252	0.261	0.275	0.252	0.284	0.268	0.208	0.248
2.0	0.296	0.322	0.747	0.422	0.262	0.281	0.295	0.260	0.298	0.276	0.220	0.259
2.25	0.302	0.337	0.754	0.427	0.285	0.301	0.313	0.270	0.306	0.287	0.235	0.266
2.5	0.318	0.353	0.767	0.432	0.316	0.320	0.331	0.280	0.315	0.298	0.250	0.272
2.75	0.333	0.373	0.773	0.438	0.331	0.339	0.350	0.302	0.340	0.319	0.271	0.294
3.0	0.349	0.393	0.778	0.444	0.342	0.358	0.370	0.324	0.365	0.340	0.292	0.316
3.25	0.373	0.415	0.789	0.451	0.367	0.378	0.392	0.337	0.383	0.353	0.316	0.331
3.5	0.398	0.437	0.799	0.457	0.376	0.397	0.413	0.350	0.401	0.367	0.340	0.346

Physical constants that, presumably, may be considered as functions of the R_F, are the actual dimensions of the ion. If the estimation proves difficult in the considered medium, (a homogeneous system of three components in which interactions take place amongst single components and ionic species), the dimensions could be approximately referred to the ionic radii.

When the above values of R_F are taken in function of the ionic radii, it appears that: (a) in the sequence: Zn, Cd, Hg, the R_F values are an increasing function of the ionic radius; (b) in the sequence: Li, Na, K, Cs, the R_F values are an increasing function of the ionic radius, with the exception of the value obtained for Li ion; (c) in the sequence: Be, Mg, Ca, Sr, Ba the highest R_F value is reached in the case of Mg, the lowest in the case of the Sr ion. A similar trend can be observed when the R_F values are taken in function of physical properties which depend on ionic radius, as, for instance, the spherical surface, the charge density and the diffusion rate which results in a decreasing function of the charge density.

The function giving the dependence of the ionic dimensions on the R_F does not appear to be a linear one. Factors to be taken in account are: the hydration of the ion and the partial ionic volume which, as is well known, are affected by phenomena of electrostriction that could be attributed to a contraction either of the ionic cloud thickness or of the distance of the ion-dipole bond.

An electrostrictive effect, which is particularly strong with alkaline-earth ions, could provoke a variation on the molar partial volume and, consequently, on the dimension of the solvated ion and on its mobilility (R_F). The Mg ion, in fact, which gives evident phenomena of electrostriction, has an abnormal position also in the (c) sequence. The same effect could probably explain the abnormal position taken by the Li ion.

SUMMARY

The radial paper chromatography of some metals: Zn, Cd, Hg; Li, Na, K, Cs; Be, Mg, Ca, Sr, Ba, carried out using as mobile phase the upper layer of *n*-butanol-water-nitric acid mixtures of increasing acidity, shows that,

1. the phenomenon of the deepening of the colour towards the external edge of the chromatogram is not to be attributed to the presence and the nature of the complex-forming agent;
2. the ionic mobility does not always result in a linear function of the ionic radius. This behaviour results from the interaction of various factors capable of provoking a variation of the dimensions of the solvated ion and consequently of its mobility.

RÉSUMÉ

La chromatographie circulaire sur papier de certains cations, appartenant au même groupe du système périodique: Zn, Cd, Hg; Li, Na, K, Cs; Be, Mg, Ca, Sr, Ba, effectuée en utilisant comme éluant la couche supérieure de mélanges *n*-butanol-eau-acide nitrique, d'acidité croissante, a montré que:

1. l'augmentation d'intensité de la coloration sur les bords des chromatogrammes (déjà mise en évidence dans des conditions différentes) n'est pas due à la présence et à la nature du réactif complexant;
2. la mobilité ionique n'est pas toujours fonction linéaire du rayon ionique. Ceci est dû à l'action de divers facteurs pouvant modifier les dimensions des ions solvatés et, par conséquent, leur mobilité.

ZUSAMMENFASSUNG

Zirkularchromatographische Untersuchungen der Metalle Zn, Cd, Hg; Li, Na, K, Cs; Be, Mg, Ca, Sr, Ba unter Benutzung der oberen Schichte von *n*-Butanol-Wasser-Salpetersäure-Mischungen von steigendem Säuregrad als Entwicklungsflüssigkeit haben gezeigt dass:

1. die Erscheinung der Farbvertiefung in der äusseren Zone des Chromatogramms nicht auf die Gegenwart und die Natur des komplexierenden Reagenzes zurückzuführen ist;
2. die Ionenbeweglichkeit nicht immer eine lineäre Funktion des Ionenradius ist. Dies kann durch das Zusammenspiel verschiedener Faktoren erklärt werden, welche die Dimensionen und deshalb die Beweglichkeit des solvatierten Ions beeinflussen.

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PAPER CHROMATOGRAPHY OF INORGANIC IONS

XIII. THE SEPARATION OF NON-COMPLEXED RARE EARTH IONS

by

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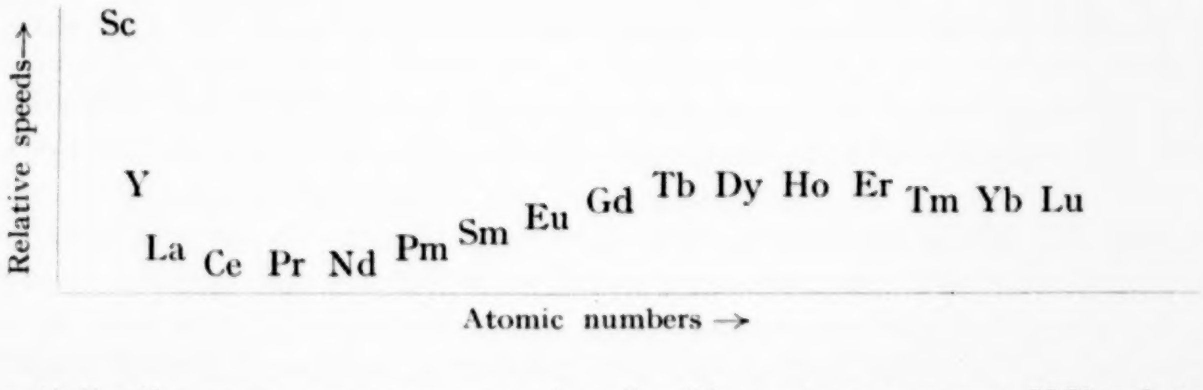
INTRODUCTION

Several publications on the paper chromatography of rare earth ions have shown that complete separations are not possible in a single development. However small R_F value differences between the rare earths were noted in many solvents[1] and GÖTTE AND PÄTZE[2] even recorded partial separations of tracer Ce-Y mixtures. The latter publication has led us to attempt descending development with the solvent dripping off the paper for several days. In a preliminary note[3] the separation Ce—Pm—Eu as well as general observations on the sequences of some rare earths were recorded. In this paper we propose to discuss the behaviour of all rare earth elements in several polar solvent mixtures containing HCl.

DISCUSSION

Using descending development and running the solvent off the paper, we had demonstrated the separability of such pairs of rare earths as La—Y, La—Dy and La—Yb using one solvent originally proposed by GÖTTE AND PÄTZE[2] for fission products, namely ethanol containing 30% 2*N* HCl. As the R_F values are rather high we later preferred to employ a mixture of ethanol-10% 2*N* HCl with a development of one week. As mentioned before[3] the sequence of the rare earths is not that of their atomic numbers. The sequence may be best expressed as below since absolute R_F values cannot be measured:



Essentially the same sequence was found with acetone-aqueous HCl mixtures which were investigated so as to speed up the development.

References p. 50

As discussed in the experimental section of this paper, the efficiency of the separations may be shown by some separations of radiochemical interest: Ce–Eu–Y, Ce–Pm–Eu, Ce–La, Er–Tm or Er–Yb and Er–Lu. Scandium can also be separated completely from all rare earths[4].

The results here reported have not solved the problem of a rare earth analysis capable of separating all the rare earths in an unknown mixture. It has however contributed to the methods of purification and identification of certain mixtures or fractions. A new sequence of the free ions has also been noted. In all cases carrier-free isotopes did not behave differently to "macro" amounts.

EXPERIMENTAL WORK

Strips of Whatman No. 1 paper 15 cm × 60 cm were cut zig-zag at one end and spots of rare earth chloride solutions (approx. 1% in N/10 HCl) were applied to the paper 20 cm from the other end. The descending development was carried out in an all-glass container fitted with a glass trough. It was found best to apply the sample from a capillary as a thin line one cm long. Usually five or six spots could be run side by side on the same sheet of paper. After development for the required time the chromatogram was air-dried and dipped into an ammoniacal alcoholic solution of 8-hydroxyquinoline (freshly prepared) and viewed under ultra-violet light. La, Y, Sc, Er and Lu yield yellow or green fluorescent spots while all other rare earths yield brown or black spots. Viewed in daylight all spots appear pale yellow and darken in a few days to an indistinct brown colour. Cerium(III) usually yields a brown spot a few minutes after reacting with the reagent.

The first solvent studied in detail after the preliminary survey was ethanol containing 10% 2N HCl.

To visualize the order and show the difficulty of determining exact differences Fig. 1 shows the spots on three paper strips running side by side. By using Sm as the reference substance in strips i and ii, it can be shown that both chromatograms were developed for the same distance. A similar reference chromatogram enables us to place strip iii in relation to strip ii.

It appeared that the best separations of adjacent rare earths would be in the region Pm-Sm-Eu-Gd-Tb and Er-Tm while no separations appear possible in the groups Ce-Pr-Nd and Dy-Ho-Er-Y. Scandium moves rapidly and is separated completely from all rare earths as shown in Fig. 2.

While we have already found applications for this technique in the separation of long half-life Pm isotopes it appeared desirable to us to look for faster solvents with otherwise similar properties. Acetone containing water and HCl is already well known for numerous separations of transition metals and flows faster than the ethanol solvent used. Preliminary work with different

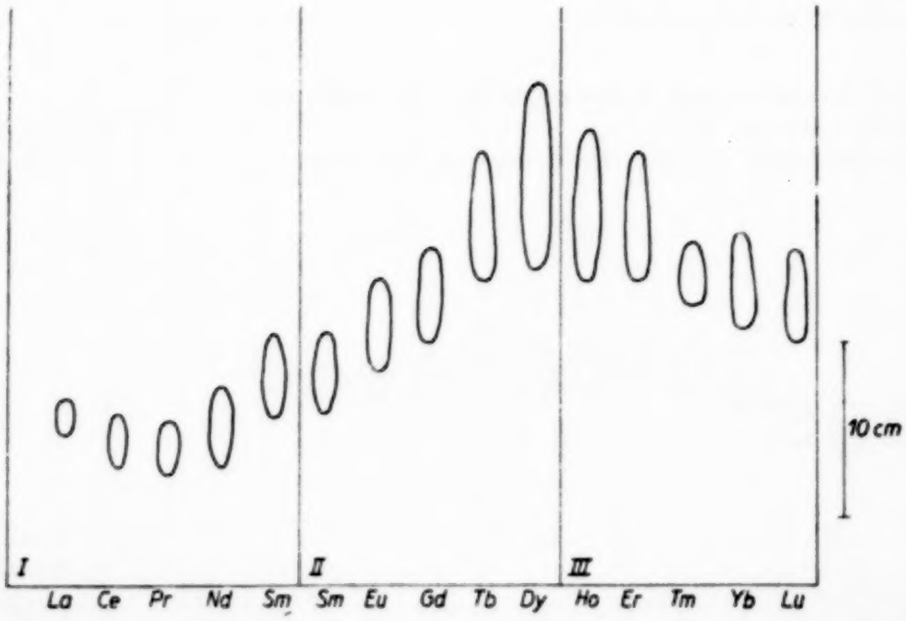


Fig. 1. Rare earth chlorides developed for 1 week with ethanol-10% 2N HCl placed in order of atomic numbers.

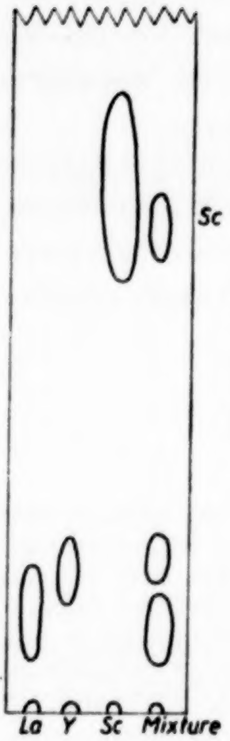


Fig. 2. Separation of scandium, yttrium and lanthanum.
Solvent: ethanol containing 10% $2N$ HCl.
Time of development: 3 days.
Reagent: 8-hydroxyquinoline in ammoniacal ethanol.

mixtures is tabulated in Fig. 3 where the spread of R_F differences between various rare earths is shown by the vertical lines. The mixture acetone-35% $2N$ HCl appeared to give the best resolution with reasonable speed of development. Several series of chromatograms were carried out with this solvent, developing for 20-24 h. The sequence of movement was determined and checked by running several chromatograms with high and low atomic number rare earths. These results are shown in Fig. 4. The possible separations were then tried by mixing the suitable rare earths and running them side by side with the pure solutions. Fig. 5, 6, 7 show the results obtained. Finally several carrier-free isotopes were chromatographed to determine whether the carrier-free tracer leaves an adsorption trail. A ^{91}Y preparation obtained from Chatillon gave two rather well separated peaks as shown in Fig. 8. The first of these was identified as a ^{144}Ce impurity by its radiation characteristics while the second was identified as the desired ^{91}Y isotope. The radiation characteristics of the Eu isotopes of fission were also found in the area of overlapping of the two zones. As only broad bands of the chromatogram were examined it was impossible to tell if these were completely separated from Ce and Y. This result suggests one immediate application of this method namely the control of ion-exchange column eluates of fission products prior to mixing of the fractions. For this purpose, if not also for the entire separation of the fission rare earths, it seems to be faster and does not require the control nor the apparatus of an ion exchange column.

A neutron irradiated Eu preparation was also available in the laboratory and was run side by side with the Ce and the Y tracers. Its activity distribution is shown in Fig. 9. From the relative positions of the peaks a ready differentiation of the main long-lived fission rare earths can thus be carried out.

Some work was also done with acetone containing 10% $2N$ HCl as solvent. The sequence is the same as in the other two solvents and the movement of the ions is rather slow. A development of one week yielded separations inferior to those with ethanol containing 10% $2N$ HCl.

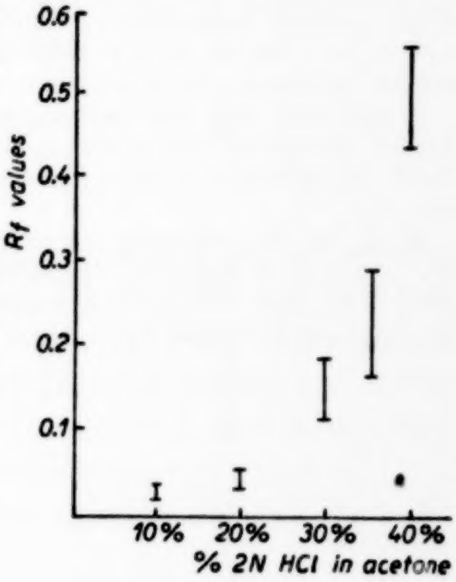


Fig. 3. R_F value trend of rare earth chlorides in mixtures of acetone and $2N$ HCl.
I shows the limits of the R_F values of the ions.

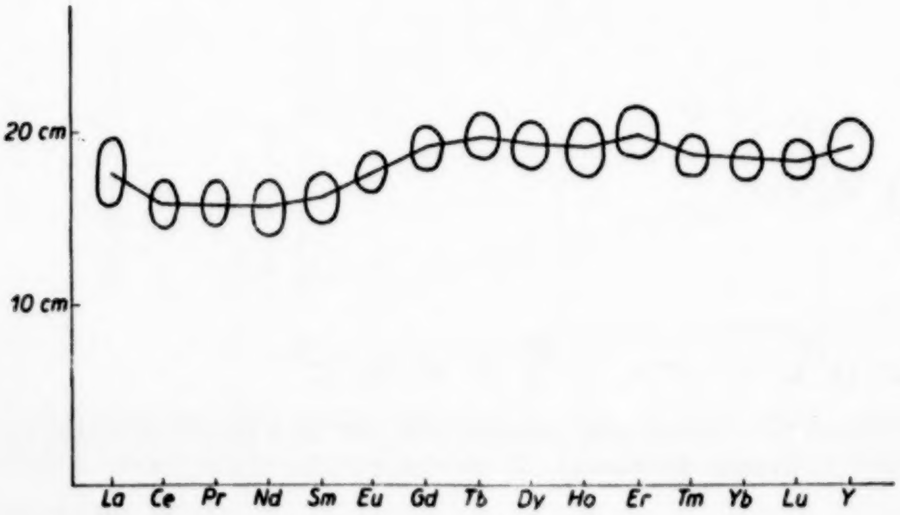


Fig. 4. Rare earth chlorides developed for 20 hours with acetone containing 35% $2N$ HCl placed in the order of atomic numbers.

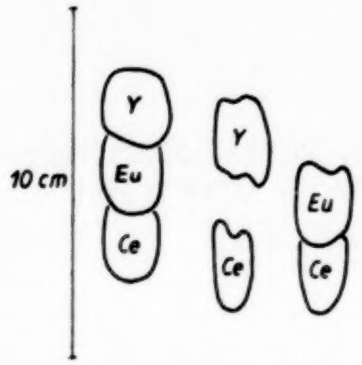

10 cm
Y
Eu
Ce
Y
Ce
Eu
Ce

Fig. 5. Separations of Y-Eu-Ce, Y-Ce and Eu-Ce with acetone containing 35% 2*N* HCl for 20 hours.

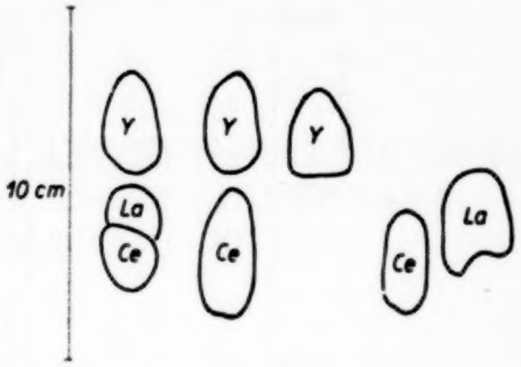

10 cm
Y
La
Ce
Y
Ce
Y
Ce
La

Fig. 6. Separations of Y-La-Ce, Y-Ce and solutions of Y, Ce and La developed on the same sheet with acetone containing 35% 2*N* HCl for 20 hours.

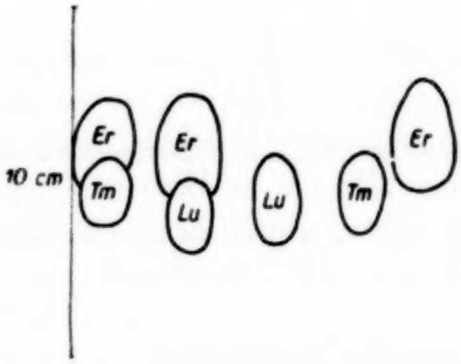

10 cm
Er
Tm
Er
Lu
Lu
Tm
Er

Fig. 7. Separations of Er-Tm and Er-Lu and solutions of Lu, Tm and Er developed on the same sheet with acetone containing 35% 2*N* HCl for 20 hours.

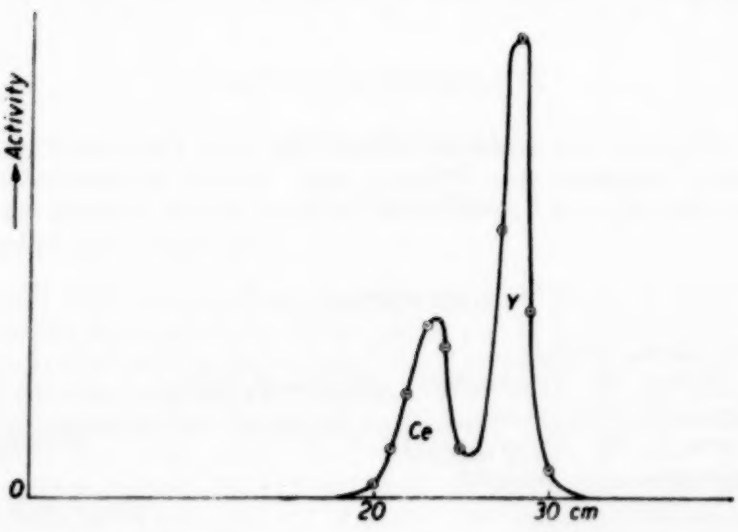


Fig. 8. Carrier-free ^{91}Y from fission products developed with acetone-35% 2*N* HCl.

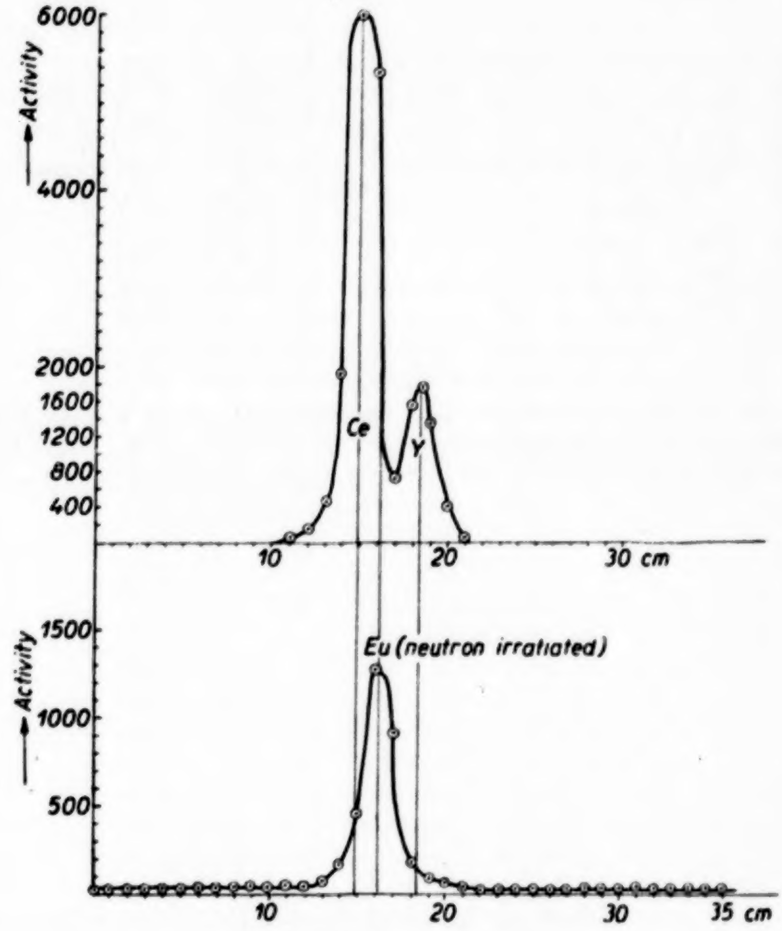


Fig. 9. Artificial mixture of ^{144}Ce and ^{91}Y with some Eu activities as impurity. Solvent: acetone-35% $2N$ HCl.

SUMMARY

The sequence of the rare earth chlorides in paper chromatography with mixtures of ethanol or acetone and aqueous HCl was established. A certain number of rare earth separations is possible.

RÉSUMÉ

L'auteur a étudié le comportement des chlorures de terres rares lors de leur chromatographie sur papier, en utilisant des mélanges d'éthanol ou d'acétone et d'acide chlorhydrique en solution aqueuse. Un certain nombre de séparations de terres rares sont possibles.

ZUSAMMENFASSUNG

Das Verhalten der Chloride der seltenen Erden bei der Papierchromatographie wurde in Gemischen von wässriger Salzsäure mit Äthanol oder Aceton untersucht und ihre Reihenfolge ermittelt. Eine gewisse Anzahl von Trennungen seltener Erden können ausgeführt werden.

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THE PREPARATION, DETECTION AND SEPARATION OF SOME VALENCY STATES OF VANADIUM AND COBALT BY PAPER CHROMATOGRAPHY

by

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INTRODUCTION

Recent work with *Neurospora crassa*[1], *Escherichia coli*[2] and higher plants[3] has shown that the enzyme nitrate reductase contains Mo, and that the element undergoes a valence change ($Mo^{VI} \rightleftharpoons Mo^{V}$) when nitrates are reduced by these organisms.

Mo is also essential for nitrogen fixation by *Azotobacter*[4], but the Mo requirement of this organism can be partly replaced by V. It was, therefore, of interest to prepare and separate the valency states of V for use in biochemical studies which are being undertaken in this laboratory.

It is well known that Co is a constituent of Vitamin B_{12}, which is produced by microorganisms, and recently it has been established by X-ray absorption analysis that the metal is present in the trivalent form[5]. Thus the separation of the valence states of Co was a useful preliminary to a study of possible valence changes of the element during microbial metabolism[6].

Independent investigations upon the separation of the valency states of several elements, including V and Co, by paper chromatography have also been carried out by POLLARD and co-workers[7,8] in the Department of Chemistry of the University of Bristol. The author is grateful to Mr. A. J. BANISTER for telling him of the work before publication.

EXPERIMENTAL

Vanadium

Preparation of vanadium solutions

V^{V} chloride solution was prepared by acidifying a solution of ammonium vanadate with 2*N* HCl, and a V^{V} sulphate solution by dissolving 4-5 g of vanadium pentoxide in a mixture of sulphuric acid (20 ml) and water (10 ml) by heating. The sulphate solution was cooled and diluted to 400-500 ml with distilled water, and filtered (Whatman No. 41 paper).

V^{IV} chloride ($VOCl_2$) solution was prepared by heating vanadium pentoxide with hydrochloric acid (d = 1.18) until the concentrated solution ceased to give a V^{V} spot when analysed by paper-strip chromatography (see below). A V^{IV} sulphate solution was prepared by dissolving 4 g of vanadyl sulphate ($VOSO_4.2H_2O$) in 500 ml of water and adding 2 ml sulphuric acid (d = 1.84), or by electrolytic reduction of V^{V} sulphate solution using Pt electrodes and a current of 6-7 A in a cell with a porous anode chamber as described by WARDLAW AND SYLVESTER[9].

V^{III} solutions were made by the following methods:

(a) V metal powder was heated with hydrochloric acid (d = 1.18), and the green solution diluted with ethanol, filtered and evaporated under reduced pressure from a water bath or at ordinary pressure in a slow stream of CO_2. The prepared solution contained Fe (as $FeCl_2$) as a contaminant from the vanadium metal employed.

(b) Reduction of an acid V^{IV} solution by zinc dust, followed by the removal of Zn^{+2} ions by chromatography, using an eluant consisting of: ethanol 100 ml, ether 100 ml, hydrochloric acid (d = 1.18) 20 ml. Then 2 g of $VOSO_4.2H_2O$, were dissolved in 20 ml of water, and the solution mixed with 40 ml of eluant. The mixture was left in contact with zinc dust with occasional agitation until the solution was blue-green or blue in colour and reduced 0.5% copper sulphate to copper (due to V^{II}). Excess of zinc dust was removed by filtration. A cellulose column 45-50 cm in length and 3.5 cm in diameter was prepared by packing a suspension of Whatman cellulose in ethanol under compressed air in the usual way. A quantity of pure eluant, followed by a solution of fuchsin in the eluant were allowed to soak into the cellulose in turn. The zinc-reduced vanadium solution was then placed on the column, and when this had sunk into the cellulose a 500 ml reservoir of eluant was inverted into the top of the column, and elution allowed to proceed. The fuchsin band together with Zn^{+2} ions moved ahead of the vanadium, and was rejected after breakthrough. The vanadium fraction was collected when the eluate commenced to reduce sodium molybdate solution to "molybdenum blue". During the run V^{II} was continually oxidized to V^{III}, which moved ahead of the former, and by the time the fraction had been collected all the vanadium was in the trivalent state. The eluate was concentrated by distillation from a water-bath under reduced pressure or at ordinary pressure in a stream of CO_2. Paper-strip analyses, using the same eluant, were performed upon the concentrated eluate fractions. The strips were developed by dipping them into a solution of oxine in ether and allowing them to dry in air. R_F values were 0.24 for V^{III} (rusty brown spot) and 0.94 for Zn^{II} (yellow fluorescence over ammonia in u.v. light[10]). Zinc was found to be concentrated in the initial fuchsin-coloured fraction and absent from the V^{III} fraction.

(c) An acid V^{V} or V^{IV} sulphate solution was prepared and electrolysed as described above until a *slight* precipitate of copper was obtained (due to the presence of V^{II}) when a few drops of the catholyte was added to 1-2 ml of 0.5% w/v solution of copper sulphate. On standing, the trace of divalent vanadium soon oxidized.

(d) V metal powder was heated in a stream of Br_2 vapour carried by dry CO_2, and the black sublimate of VBr_3 was dissolved in a warm mixture of acetone and water (80 vols : 20 vols).

V^{II} solutions were prepared by reducing solutions of the other valencies, containing a small excess of hydrochloric acid, with Zn dust. When excess of Zn was removed by filtration, the lavender solution soon oxidized, and was deemed too unstable for experiments of any duration.

Reducing power of the valencies

A few drops of the chloride solution of each valency were added in turn to 2-3 ml of the following reagent solutions in separate test tubes (a) 2% sodium molybdate to which one tenth of the volume of 2*N* HCl had been added to give a pale yellow colour, (b) 0.5% w/v copper sulphate, (c) mercuric chloride (saturated solution), (d) potassium nitrate (0.1*M*) with sulphanilamide (1% in *N* HCl) and N-(1 naphthyl) ethylenediamine dihydrochloride (0.001%)[11]. Results are set out in Table I.

TABLE I

Reagent solution	V^{V}	V^{IV}	V^{III}	V^{II}
(a)	no action	no action	blue (Mo blue)	blue (Mo blue)
(b)	no action	no action	*white precipitate of Cu_2Cl_2	brown precipitate of Cu
(c)	no action	no action	*white precipitate of Hg_2Cl_2	black or grey precipitate of Hg
(d)	no reduction	no reduction	pink, due to reduction of NO_3^-	pink, due to reduction of NO_3^-

* In strongly acid solution precipitation is inhibited; buffering with sodium acetate is then advisable.

V^{III} appeared to reduce Cu^{+2} and Hg^{+2} ions to the univalent state only.

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Estimation of the strength of vanadium solutions

The method of TALVITIE[12] using 8-hydroxyquinoline was modified, and the estimations were carried out in the absence of iron, which caused serious interference and could not be satisfactorily removed by chemical extraction methods.

A standard solution of V^V containing 1000 μg V per ml was prepared by warming 0.2294 g of "AnalaR" ammonium vanadate with water, and adding 2*N* sodium hydroxide until a clear solution was obtained. The solution was then acidified with 10 ml of 2*N* HCl* and diluted to 100 ml with distilled water. Volumes of this standard ranging from 0.1 ml to 0.7 ml were then mixed with 1 ml of 2*N* HCl and shaken with 50 ml aliquots of 1% w/v 8-hydroxyquinoline in pure chloroform at two minute intervals for 15 minutes. The chloroform extracts were then filtered, and a calibration curve obtained on a Hilger "Spekker" absorptiometer using Ilford No. 604 green filters and a drum setting of 1.30.

The use of a phthalate buffer as recommended by TALVITIE[12], was found to suppress the colour of the vanadium oxine complex under the conditions employed here, and so was omitted in the estimations.

The strengths of V^{IV} and V^{III} solutions were determined by digesting measured aliquots (0.1-0.5 ml) with a mixture of nitric acid (20 ml), sulphuric acid (2 ml) and perchloric acid (5 ml) until most of the latter had been fumed off. The resulting orange-yellow digest containing the vanadium in the pentavalent state was cooled, mixed with 50 ml of water and treated with sodium hydroxide solution until just alkaline to phenolphthalein. The mixture was then neutralized with 2*N* HCl and 1 ml of the acid added in excess. The solution was allowed to stand for 10-15 minutes until it was colourless and the vanadium was estimated by extraction with a 1% w/v solution of oxine in chloroform as described above. The error obtained in the determination of duplicate aliquots (0.05 ml) of a V^{III} solution containing 9700 μg V per ml was 0.6%.

Separation of the valencies by paper-chromatography

Valencies differing in charge by more than 1 were found to interact with one another, and so separations were achieved between V^V and V^{IV} and between V^{IV} and V^{III}. Downward chromatography upon acid-washed Whatman No. 1 paper-strips was employed for the separations.

Eluants containing ether have been successfully used by POLLARD *et al.*[8], and in this work those containing acetone and ether were employed. The very volatile nature of these solvents rendered the reproduction of results difficult at times, and it was sometimes observed that the best results and the most compact spots were obtained when a small chromatography jar (30 cm × 12 cm diameter) was used without the preliminary equilibration of the air in the jar with the eluant vapour. Previous equilibration had the effect of reducing movement and causing tailing. This effect could also be produced by increasing the acetone or ether content of the eluant and it is suggested that the escape of vapour from the trough, followed by its adhesion to the wet strip increased the concentration of the volatile constituent on the strip during the run, and caused the detrimental effect upon the separations. Chromatograms were developed by dipping them into a solution of 8-hydroxyquinoline in ether and allowing them to dry in air. A black spot appeared almost at once for V^V, a dark yellowish-brown one for V^{IV} gradually turning black, and a rust-coloured spot for V^{III} which turned black over a period of several hours.

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* A yellow colour at this stage was allowed to fade before proceeding, in order to avoid low results.

V^{III} spots became blue or yellow upon chromatograms sprayed with acidified sodium molybdate or potassium thiocyanate solutions respectively. The corresponding colours for V^{IV} spots were pale greenish brown and pale blue.

Solvent mixtures recommended for the separations of the valencies with approximate R_F values are given in Table II.

TABLE II

Valencies separated		*Solvent mixture*		*R_F values (approx.)*	*Notes*
V^V and V^{IV}	(a)	Ethanol	: 50 ml	V^V 0.50	Solvent (a) preferred because of the less volatile nature of the organic constituent.
		acetic acid	: 20 ml	V^{IV} 0.80	
		20% sodium acetate solution	: 30 ml	(20 cm run)	
	(b)	acetone	: 84 ml	V^V 0.40	Replacement of the ether by isopropyl ether gave inferior results (c.f. cobalt separations below).
		ether	: 42 ml	V^{IV} 0.70	
		acetic acid	: 25 ml	(20 cm run)	
		20% sodium acetate solution	: 50 ml		
V^{IV} and V^{III}	(c)	ethanol	: 50 ml	V^{IV} 0.68	(c) preferred to (d). It was essential to buffer the vanadium solutions to pH 6-7 with 40% sodium acetate to get a satisfactory separation.
		acetic acid	: 5 ml	V^{III} 0.97	
		40% sodium acetate solution	: 10 ml	(15 cm run)	
	(d)	acetone	: 50 ml	V^{IV} 0.64	
		acetic acid	: 10 ml	V^{III} 0.97	
		40% sodium acetate solution	: 5 ml	(17.5 cm run)	

Quantitative investigation of V^V-V^{IV} separations

Chromatograms loaded with a mixture of 0.1 ml of V^V solution (3480 µg V per ml) and 0.1 ml of V^{IV} solution (3530 µg V per ml) were run in solvent mixture (b) (see Table II). An attached "pilot" strip was run alongside each of the main chromatograms in the usual way[13]. After the run the chromatograms were dried and the pilot strips cut off and developed by dipping them into an ethereal solution of 8-hydroxyquinoline. The vanadium-bearing bands were then cut out from the main chromatograms and digested in a hot mixture of nitric acid (50 ml) and sulphuric acid (5 ml) until all solid matter had disappeared. Perchloric acid (5 ml) was then added and the mixture heated until nearly all of the latter had been fumed off. After cooling, the vanadium estimation was carried out as described previously. Two typical results are given below in Table III. A blank chromatogram was treated as one bearing vanadium. Bands of the same area as the valency zones were excised and digested, and allowance made for the readings in the vanadium analyses.

TABLE III

	V^V put on	*V recovered*	*V^{IV} put on*	*V recovered*
Experiment 1	348 µg	372 µg	353 µg	326 µg
Experiment 2	348 ,,	360 ,,	353 ,,	343 ,,

It was noted that a faint yellow tail was usually present behind the V^V spots. This was presumed to be colloidal vanadium pentoxide which had been precipitated from the acidified vanadate solution by the buffering action of the sodium acetate

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in the solvent mixture and so the part of the main chromatogram bearing the tail was always included in the V^{V} digest. No backward tail was produced with V^{IV} (or V^{III}) spots. Exclusion of sodium acetate from the solvent mixture gave inferior separations of V^{V} and V^{IV}.

The results, which were not regarded as being very satisfactory, suggested that the high values usually obtained for V^{V} might be due to some adsorption of V^{IV} (vanadyl) ions by the precipitated vanadium pentoxide tail which also caused low values for V^{IV}. It is impossible to get a truly representative "blank" determination as another sheet of filter paper has to be used, and this is suggested as being another source of error.

V^{III} solutions underwent oxidation too readily on the chromatogram to permit a separation from V^{IV} to be investigated quantitatively.

Interaction of vanadium and molybdenum valencies

It was necessary, prior to biological application, to determine interactions between the valency-states of V and Mo. These tests were carried out using chloride solutions, and were based upon the reducing properties of the V valencies given in Table I, the reactions of Mo valencies with potassium thiocyanate, and the fact that copper sulphate and mercuric chloride were reduced to cuprous or mercurous chloride by Mo^{III} but were unaffected by Mo^{V}. The conclusions drawn from these tests are summarized in Table IV.

TABLE IV

(— no action, + interaction)

	V^{V}	V^{IV}	V^{III}	V^{II}
Mo^{VI}	—	—	+	+
Mo^{V}	+	—	—	+
Mo^{III}	+	—	—	—

Cobalt

For biological purposes it was desired that the Co in the valency solutions should not be in the form of co-ordinate complexes. As the Co^{+3} ion itself is unstable, a solution of the weakly-complexed acetate was used for the work.

Preparation of cobalt solutions

Co^{II}. Cobaltous acetate tetrahydrate (1.0 g) was dissolved in water, 1 ml of glacial acetic acid was added and the volume made up to 100 ml with distilled water. This solution contains 2370 μg of Co per ml.

Co^{III}. 50 ml of ice-cold Co^{II} solution (prepared as above) was added gradually with shaking to an ice-cold mixture of saturated potassium bicarbonate solution (9 ml) and 100 volume hydrogen peroxide (1.5 ml). Acetic acid (2 ml) was added, and when effervescence had ceased the solution was diluted to 100 ml with distilled water. This solution contained 1185 μg Co per ml.

Estimation of the strength of Co solutions. The strength of both valency solutions was estimated colorimetrically as the blue thiocyanate compound (Co^{II}) in acetone.

Reagents required

1. 80% *acetone*. A mixture of acetone 80 vols. and water 20 vols.

2. *Thiocyanic acid*. 40 ml of hydrochloric acid (d = 1.18) was mixed with an ice-cold solution of potassium thiocyanate (40 g) in water (40 ml). Acetone (400 ml) was added to the mixture (which was kept ice-cold during the addition) and after being allowed to stand in the refrigerator for an hour, the precipitated potassium chloride was removed by filtration through a Whatman No. 41 filter paper.

3. *Standard Co solution*. 0.4034 g of AnalaR cobaltous chloride hexahydrate was dissolved in distilled water, and the solution diluted to 100 ml in a graduated flask. This solution contains 1000 μg of Co per ml.

A Hilger "Spekker" absorptiometer was calibrated by mixing volumes of this standard solution ranging from 0.2 ml to 2.0 ml with 10 ml of thiocyanic acid reagent and diluting to 50 ml with 80% acetone. Readings were obtained on the drum using Ilford No. 607 orange filters and a drum-setting of 1.30. The Co concentration range in the acetone solutions was 4-40 μg per ml.

The strength of the Co^{II} acetate solution was checked by treating an 0.5 ml aliquot in the manner described. A value of 2375 μg Co per ml was obtained. A similar check was performed upon 0.5 ml of the Co^{III} acetate solution giving a value of 1187 μg Co per ml.

The presence of hydrochloric acid was found to suppress the colour of the cobalt thiocyanate (presumably because of dissociation) and iron, which caused serious interference, could not be effectively suppressed by stannous chloride in the acetone medium employed. A possible explanation for this is that stannous chloride is present in acetone as a covalent compound, thereby rendering the reducing power of the Sn^{II} ion ineffective.

Chromatographic separation of the valency states

For qualitative experiments more concentrated Co^{II} and Co^{III} solutions were prepared. For a Co^{II} solution 10 g of cobaltous acetate tetrahydrate and 5 ml of acetic acid were dissolved in distilled water, finally diluting to 50 ml and filtering. To prepare the Co^{III} solution, 10 ml of this Co^{II} solution (ice-cold) was slowly added to an ice-cold mixture of saturated potassium bicarbonate solution (35 ml) and 100 vol. hydrogen peroxide (5 ml), followed by 6 ml of glacial acetic acid. Freshly prepared Co^{III} acetate solution, when analysed by paper-strip chromatography (see below) gave a very faint Co^{II} spot.

When it was desired to remove residual hydrogen peroxide from the Co^{III} solution immediately, a small quantity of a suspension of metallic silver (prepared by mixing solutions of silver nitrate, sodium hydroxide and hydrogen peroxide, and centrifuging and washing the precipitate) was added; the mixture was shaken for a short time and then filtered from the silver. By allowing hydrogen peroxide solutions of different strength to stand over precipitated silver, an approximate minimum concentration of 1 part by weight of H_2O_2 in 10,000 volumes of solution could be detected by the escape of oxygen bubbles from the surface of the metal.

Spots of the mixed valency solution were run on acid washed Whatman No. 1 paper strips by downward chromatography.

The eluant used was prepared by warming powdered magnesium acetate (1.5 g) with ethanol (60 ml) and acetic acid (3.5 ml) until the solid had dissolved. The solution was cooled, 30 ml of diethyl ether was added, and the mixture filtered and stored in the refrigerator. The diethyl ether could be replaced by 30 ml of iso-propyl ether with virtually the same results, but with *n*-butyl- or *n*-amyl ether, the movement of the spots was reduced and resolutions were inferior. When the *iso*-propyl ether : ethanol ratio in the eluant was increased to 40 : 50 or 50 : 40, good results were obtained, provided that the separations were carried out on unwashed Whatman No. 1 strips. An increase in the ethereal constituent imparts a swifter flow-rate to the eluant, and this seems to be enhanced by the acid-washing of the paper. Consequently, the flow is too great, and poor resolutions are obtained. The Co separations, like the vanadium ones (*q.v.*), were sometimes impaired by the previous saturation of the air in the chromatography jar with the eluant vapour.

The inclusion of magnesium acetate in the eluants improved the separations and was prompted by the discovery of POLLARD and co-workers[14] that the addition of ammonium salts of fatty acids to solvents used for the separation of alkaline earth elements resulted in better resolutions. Ammonium or potassium acetate was not sufficiently soluble in the eluants employed for the cobalt separations to permit the use of either of these salts, and so magnesium acetate was employed instead.

The dried strips were developed by dipping them into either a solution of oxine in ether and drying in air (yellow spots) or into the thiocyanic acid reagent (blue spots). A spray of potassium iodide in dilute sulphuric acid detects Co^{III} as a brown spot, due to the liberation of iodine.

When the strips were sprayed with a 0.2% solution of 2-nitroso-1-naphthol-4-sulphonic acid in 50% ethanol, which has been found to be a very sensitive detecting reagent for cobalt by POLLARD *et al.*[15], it was observed that the Co^{III} zone tailed back to the starting point. The approximate R_F values of the main spots were 0.9-0.95 for Co^{III} and 0.55-0.60 for Co^{II} (13-14 cm run).

A quantitative investigation was made by the usual method[13]. The Co valency bands were ashed with nitric and perchloric acid, and then fumed to dryness with hydrochloric acid. The residues were taken up in a few drops of water, 10 ml of thiocyanic acid reagent was added, and the solution diluted to 50 ml with 80% acetone. The Co concentrations were then measured colorimetrically on the "Spekker". A blank chromatogram was treated in a parallel manner. The values for the Co^{II} fraction were always high, and those for the Co^{III} fraction low, due presumably to the gradual reduction of the latter on the paper during the run.

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SUMMARY

Solutions containing penta-, tetra- or trivalent vanadium were prepared and their vanadium strength estimated. The reducing power of all the vanadium valencies upon Cu^{+2} and Hg^{+2} salts, acidified molybdate, and nitrate was investigated. Separations between the valency states, which included a quantitative investigation of a V^{V}-V^{IV} separation, and between V^{III} and Zn by paper chromatography are described. The interaction of vanadium valencies with some Mo valency-states are summarized.

A chromatographic separation of Co^{II} and Co^{III} as acetates, including a brief quantitative investigation, is also described.

RÉSUMÉ

Des solutions, renfermant le vanadium penta-, tétra-, ou trivalent, ont été préparées; la teneur en vanadium de ces solutions a ensuite été déterminée. Le pouvoir réducteur du vanadium, à ces différentes valences, sur les sels de Cu^{+2} et de Hg^{+2}, le molybdate en solution acide et le nitrate, a été examiné. Des séparations entre les différents stades de valence (comprenant une recherche de séparation quantitative de V^{V}-V^{IV}) et entre V^{III}-Zn par chromatographie sur papier sont décrites. Les interactions du vanadium et du molybdène, à différentes valences, sont signalées.

Une séparation chromatographique de Co^{II}-Co^{III} comme acétates, avec une brève étude quantitative, est également décrite.

ZUSAMMENFASSUNG

Fünf-, vier- oder dreiwertiges Vanadin enthaltende Lösungen wurden hergestellt und ihr Vanadingehalt bestimmt. Das Reduktionsvermögen der verschiedenen Wertigkeiten des Vanadins gegen Salze von Cu^{+2} und Hg^{+2} sowie gegen Molybdat in saurer Lösung und gegen Nitrat wurde untersucht. Papierchromatographische Trennungen der verschiedenen Wertigkeitsstufen (mit Inbegriff einer quantitativen Untersuchung der Trennung V^{V}-V^{IV}), sowie von V^{III}-Zn wurden beschrieben. Die Wechselwirkungen zwischen den verschiedenen Wertigkeiten des Vanadins und einigen Wertigkeiten des Molybdäns wurden zusammengefasst.

Eine chromatographische Trennung der Acetate von Co^{II} und Co^{III}, sowie eine kurze quantitative Untersuchung dieser Trennung wurden ebenfalls beschrieben.

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ÉTUDE DU DOSAGE TURBIDIMÉTRIQUE DU BARYUM

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Au cours d'une étude sur les ferrocyanures de baryum, nous avons été amenée à définir les conditions dans lesquelles il convenait de se placer pour effectuer le dosage du baryum par turbidimétrie de son sulfate, en stabilisant sa suspension par un colloïde protecteur.

Dans sa thèse de Pharmacie, Mlle LIANDIER[1], avait envisagé le problème du dosage de l'ion SO_4^{-2} par néphélométrie dans le but de rechercher quelques applications analytiques pratiques, de certaines substances tensio-actives, en étudiant seulement le point où la courbe ne se sépare pas de la ligne droite.

Notre point de vue est tout à fait différent: nous abordons le problème général de la turbidimétrie à propos de nos dosages de l'ion Ba^{+2} et nous étudions la courbe obtenue.

Il s'agissait pour nous de déterminer quels étaient

1. Le meilleur colloïde protecteur.
2. La longueur d'onde pour laquelle la sensibilité est maximum, pour une même densité optique.
3. La quantité maximum de baryum sur laquelle pouvait être effectué le dosage.

Les déterminations ont été faites, à l'aide d'un photocolorimètre, sur les suspensions obtenues par précipitation à l'état de sulfate et dans un volume constant de 10 ml de quantités connues de baryum. Le titre de la solution de baryum utilisée était de 1 mg/ml; celui de la solution précipitante de sulfate de sodium, de 20 mg/ml.

Choix du colloïde protecteur

Nous nous sommes inspirée d'une étude sur le dosage colorimétrique du magnésium par le jaune thiazole, qui avait indiqué que la gélatine à 0.1% donnait de meilleurs résultats que l'amidon, l'agar-agar et divers détergents.

Bien que la gélatine ne constitue pas le meilleur colloïde protecteur, comme nous le verrons par la suite, elle nous a cependant donné des résultats nettement moins défavorables que ceux enregistrés avec un détergent tel que le teepol.

La courbe D de la Fig. 2 établie avec ce détergent, dans les mêmes conditions qu'avec la gélatine, indique bien que pour une même densité optique, la sensibilité est maximum avec cette dernière.

Pour fixer la concentration optimum de notre stabilisateur, nous avons étudié sa valeur pour des solutions à 0.05, 0.1, 0.2 et 0.5 % de gélatine.

La solution à 0.05% donne une très faible stabilisation, celle à 0.2 ou celle à 0.5% ne donne pas de meilleurs résultats que celle à 0.1%; notre choix s'est donc fixé à cette dernière solution de gélatine à 0.1%.

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[1] L. LIANDIER, Thèse de Pharmacie, Toulouse, 1955.

Nous avons constaté qu'il était nécessaire d'agiter énergiquement avant la mesure et de l'effectuer rapidement.

En effet, si les lectures sont identiques lorsqu'elles sont faites immédiatement ou après une attente maximum de 1 minute, à cause de la présence du stabilisateur, il n'en est plus de même si nous attendons 5 minutes, et nous observons une légère baisse dans la graduation, baisse qui s'accroît au fur et à mesure que le temps d'attente augmente.

En opérant rapidement les résultats sont reproductibles et la méthode présente une fidélité satisfaisante.

Influence de la longueur d'onde sur la sensibilité du colorimètre

Nous avons effectué trois séries de déterminations, la première en lumière blanche, les deux autres vers les régions extrêmes du spectre soit à des longueurs d'onde moyenne de 4950 et 7000 Å.

Pour chaque série nous avons effectué les mesures sur des quantités connues et croissantes de baryum, et nous donnons ci-dessous, le tableau des valeurs que nous avons enregistrées.

TABLEAU I

Ba	*Filtre 4950* Å		*Sans filtre*	*Filtre 7000* Å	*Courbe théorique*	
mg/10 ml	*Déviations*	*Dens.opt.*	*Déviations*	*Déviations*	*Déviations*	*Dens.opt.*
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1	0.80	0.007	0.60	0.40	10.0	0.072
0.2	2.10	0.015	1.40	1.20	20.0	0.140
0.3	3.00	0.024	2.20	1.90	30.0	0.210
0.4	4.40	0.032	3.50	3.00	40.0	0.287
0.5	5.50	0.040	4.00	3.80	50.0	0.370
0.6	6.80	0.048	4.40	4.05	60.0	0.460
0.7	7.70	0.056	5.15	4.80	70.0	0.570
0.8	8.80	0.063	7.10	6.40	80.0	0.700
0.9	10.00	0.072	8.00	7.20	90.0	0.910
1.0	11.00	0.078	9.95	9.00	100.0	∞
1.5	17.00	0.120	14.60	13.40		
2.0	22.30	0.156	19.50	18.00		
2.5	28.00	0.200	24.40	22.20		
3.0	34.00	0.234	29.00	26.60		
3.5	38.00	0.275	34.20	30.60		
4.0	43.00	0.312	38.50	34.90		
4.5	47.20	0.350	42.70	39.00		
5.0	51.60	0.391	46.50	43.10		
5.5	55.30	0.427	49.20	44.80		
6.0	60.50	0.470	51.40	47.00		
6.5	63.00	0.510	53.00	48.20		
7.0	63.50	0.538	54.00	49.30		
8.00	63.55	0.540	54.80	50.00		
10.0	63.60	0.553	55.00	50.30		
20.0	63.60	0.553	55.00	50.50		

Les courbes représentatives de la déviation du colorimètre en fonction de la quantité de baryum (Fig. 1) font apparaître que:

1. La sensibilité de l'appareil est maximum pour une longueur d'onde moyenne de 4950 Å, et minimum pour une longueur d'onde moyenne de 7000 Å, la courbe obtenue en lumière blanche se trouvant entre les deux précédentes, mais plus rapprochée toutefois de celle de 7000 Å.
2. Pour des mesures effectuées avec une longueur d'onde de 4950 Å la quantité de baryum renfermée dans 10 ml de liquide, ne saurait excéder 6 mg.

Influence de la quantité de baryum sur la précision de la méthode

A côté de la courbe E représentative de la déviation du colorimètre en fonction de la densité optique (Fig. 2), nous avons tracé celle obtenue avec le baryum pour une longueur d'onde de 4950 Å.

Les deux courbes coïncident jusqu'au point *a*, correspondant à une densité optique de 0.312 obtenue avec 4 mg/10 ml de baryum. A partir de ce point, la courbe de baryum s'écarte progressivement de celle des densités optiques jusqu'au point *b*, correspondant à une quantité de baryum de 6.5 mg au-delà de laquelle le dosage du baryum par turbidimétrie, n'est plus possible.

Il résulte de ceci, que pour des quantités de baryum comprises entre 6.5 et 4 mg dans 10 ml, il faudra obligatoirement tracer expérimentalement la partie de la courbe *a*-*b*; tandis que pour des quantités renfermant de 0 à 4 mg de baryum, pour 10 ml, il suffira de se reporter à la courbe des densités optiques.

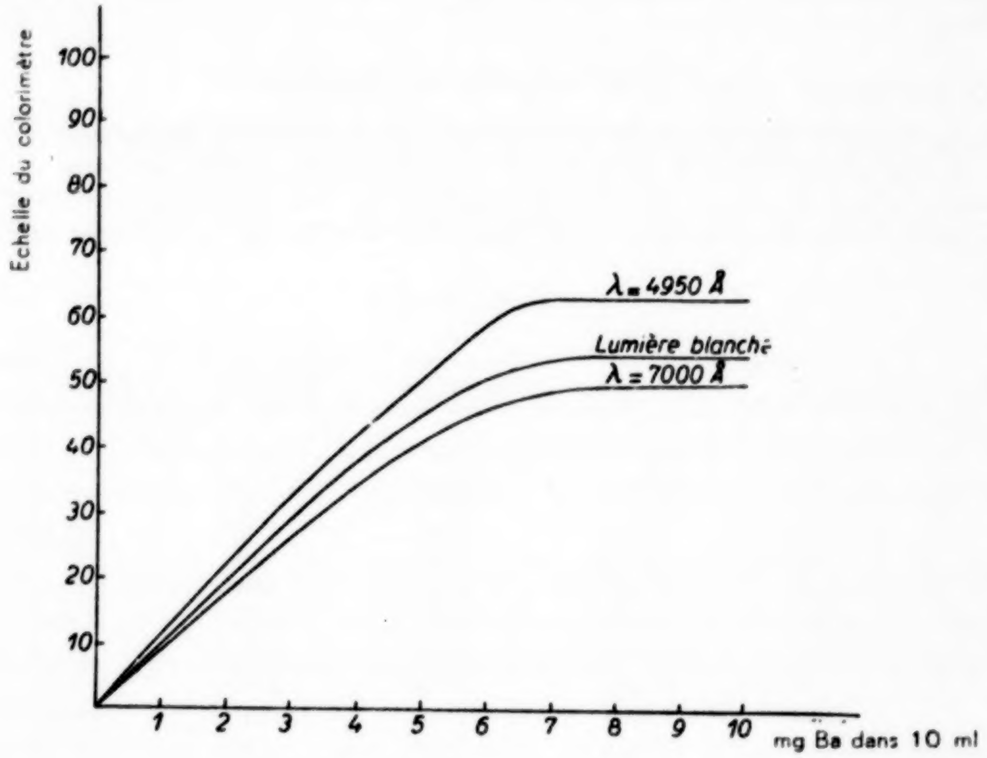

Fig. 1

D'autre part, on constate qu'en *c* la courbe du baryum devient asymptotique; si on trace une parallèle à l'axe des abscisses, cette dernière coupe la courbe des densités optiques au point *p*.

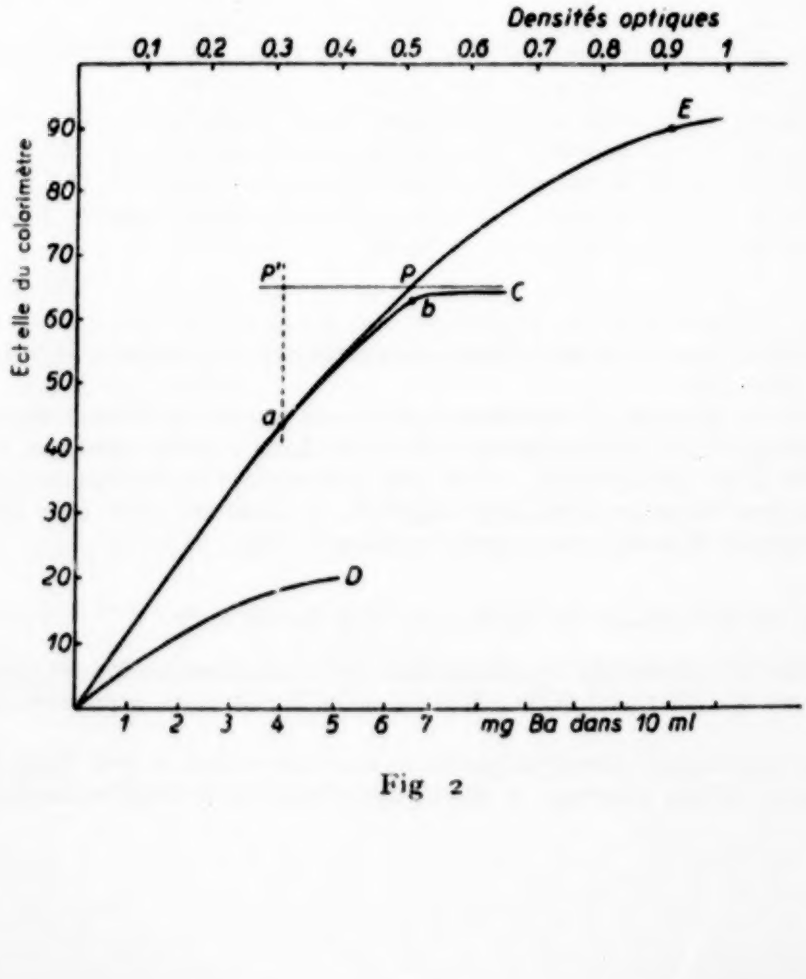

Fig 2

La distance a-p' peut être considérée comme caractéristique du pouvoir stabilisateur du colloïde, puisque pour une stabilisation idéale la courbe du baryum étant confondue avec celle des densités optiques a-p' serait nul.

Il paraît donc possible de comparer les pouvoirs stabilisateurs des colloïdes et de déterminer expérimentalement en toute certitude celui qui convient le mieux.

RÉSUMÉ

Ce travail montre les possibilités de la turbidimétrie et ses limites pour le dosage du baryum. Il suggère une méthode générale d'étude des colloïdes protecteurs.

SUMMARY

This study reveals the possibilities of turbidimetry and its limits in the estimation of barium. A general method is suggested for the study of protective colloids.

ZUSAMMENFASSUNG

Diese Arbeit zeigt die Möglichkeiten der Turbidimetrie und ihre Grenzen bei der Bestimmung von Barium. Eine allgemeine Methode zur Untersuchung der Schutzkolloide wird vorgeschlagen.

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A QUICK AND DIRECT MICRO-HETEROMETRIC DETERMINATION OF TRACES OF COPPER WITH RUBEANIC ACID IN METALS AND ALLOYS

by

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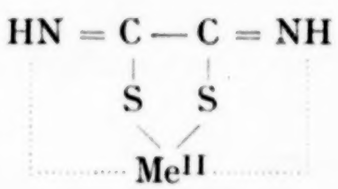
INTRODUCTION

Rubeanic acid is widely used for the spot-test analysis of traces of metals[1]. The thio-compounds formed are very insoluble and give characteristic colours. Using the reagent, one part of copper in a million parts of solution can be detected. A greenish-black precipitate or a dull green colour is produced. The extremely insoluble compound gives sols which can be determined colorimetrically. In a buffered solution, with complexing agents (such as malonic acid) added, copper can be determined in the presence of other cations. In all cases it is assumed that the organic reagent acts with a valency of two, giving a compound which can be represented as follows:



The metal thus forms a five-membered ring with sulfur atoms and additionally participates in two four-membered rings with the imido-groups. How far the four-membered rings influence the complex character of the rubeanates cannot be said with certainty.

Concerning the solubility of the rubeanates in organic reagents, it was ascertained during the course of the heterometric titrations that the insoluble lead and cadmium compounds were not precipitated from a 50% solution of dioxane, whilst the copper compound was partly dissolved in the dioxane. In contrast to these, the insoluble silver, mercury, nickel, cobalt and zinc compounds were insoluble in 50% dioxane. Copper, cobalt and nickel give brown or black precipitates whereas lead, cadmium, zinc and mercury (Hg^{II}) give either yellow (Pb, Hg) or white (Zn, Cd) precipitates. Those cations which show affinity to the imido-group are not clearly differentiated from the others. Probably the reaction between the cation and the rubeanate proceeds in two steps as follows:

$$2\ \mathrm{Cu}^{+2} + \mathrm{H_2Rub} \rightarrow [\mathrm{Cu_2Rub}]^{+2}\downarrow + 2\mathrm{H}^+ \ldots\ldots\ldots\ldots \quad (1)$$

$$[\mathrm{Cu_2Rub}]^{+2} + \mathrm{H_2Rub} \rightarrow 2\ \mathrm{CuRub}\downarrow + 2\mathrm{H}^+ \ldots\ldots\ldots\ldots \quad (2)$$

When the titration was made very rapidly the steps could only rarely be differentiated, but in many curves (when there was a longer interval after each addition of titrant) a break was obtained when half the amount of rubeanic acid had been added.

The heterometric determination of copper with rubeanic acid is very sensitive and ranks in sensitivity with other thiocompound determinations. In spite of the fact that the reaction is not specific to copper a way was found in every case of making a precise determination of traces of copper in the presence of large excesses of any bi- or polyvalent cation. The 20 ml of aqueous solution used for the analysis, contained $\sim$0.2 mg copper ($\sim 2 \cdot 10^{-4} M$) and the percentage of the latter in the total metal content was generally as low as $\sim$0.1%. With heavy metals the copper made up about 0.02%; with the light metals it amounted to 0.2%. An acetic acid solution of copper was generally used. In the presence of >99% of ferric iron, an amount of sodium acetate greater than the amount of iron (in moles) was added to assure iron-acetate complex formation. Under these conditions the determination of copper could be carried out without interference and without a reduction of sensitivity (= maximum density value).

Copper could be determined with the same sensitivity in strongly ammoniacal solutions containing, in most cases, large excesses of alkali, tartrate or citrate. These solutions were especially useful for the determination of copper in the presence of $\geqslant$99.8% of antimony or bismuth.

In all heterometric titrations of copper with rubeanic acid, difficulties, at first apparently insurmountable, were generally encountered in reading the deflection of the galvanometer. On the dropwise addition of rubeanic acid, after each addition a maximum density value was instantly obtained which however very rapidly dropped again until a constant end-value was reached after some time. A titration sometimes lasted an hour. At the theoretical end-point of the titration an abrupt and very considerable density drop occurred and the location of the end-point was, therefore, inconvenient.

This phenomenon is probably closely connected with the two-step reactions mentioned above, each of which presumably proceeds at a different velocity and each of which produces insoluble particles of a different character and stability. The disturbances occur both in acid and in ammoniacal solution, but in the latter case they are particularly difficult to overcome.

In the course of the study different supplements were added to the acetic acid solution. It was found that the addition of complexing agents such as the alkali metal salts of tripoly-, pyrophosphate, citrate or tartrate were helpful. Tripolyphosphate was most effective: constant density values were obtained from the beginning and the titration was far shorter. Unfortunately, the use of masking agents is connected with difficulties in the presence of large excesses of foreign metals. Therefore, without interfering with the composition of the analysed solution, *another* method of titration was adopted. The titrant was added dropwise and the galvanometer deflections were read as soon as the *maximum* deflection had been reached. Thus, an entire titration lasted only 3-4 minutes in an ammoniacal solution, whilst when working in acetic acid solution the titration time was somewhat longer though generally it lasted less than 10 minutes.

It is therefore advisable to determine the copper in acetic acid solution. The precision of the determination was high and in most cases the error was zero.

In the titrations presented there was 1 part of copper in about 90,000 parts of solution. As the determination of at least 1/30 of the amount of copper could be made with accuracy, it may be concluded that 1 part of copper in about 3,000,000 parts of solution can be safely determined.

METHODS AND MATERIALS

Technique

The same instrument was used and the same working conditions were observed as in previous heterometric investigations[2]. All titrations were carried out at 20° C. Variations of temperature were without effect on the accuracy of the results. In most titrations a Corning green filter No. 4010 was used.

The readings of the galvanometer gave maximum deflection in all cases almost instantly after the dropwise addition of rubeanic acid. On further waiting the maximum dropped slowly again. These latter disturbances could be avoided in the following way: the titrant was added dropwise very rapidly and the readings were made at the moment the maximum deflection was reached. All the results given in the curves and tables were obtained by this "ultra rapid" titration.

Reagents

The rubeanic acid (= dithiooxamide) was an Eastman Organic Chemicals reagent "for chemical purposes". It was dissolved in ethylalcohol. The stock solution which was 0.02M was then diluted

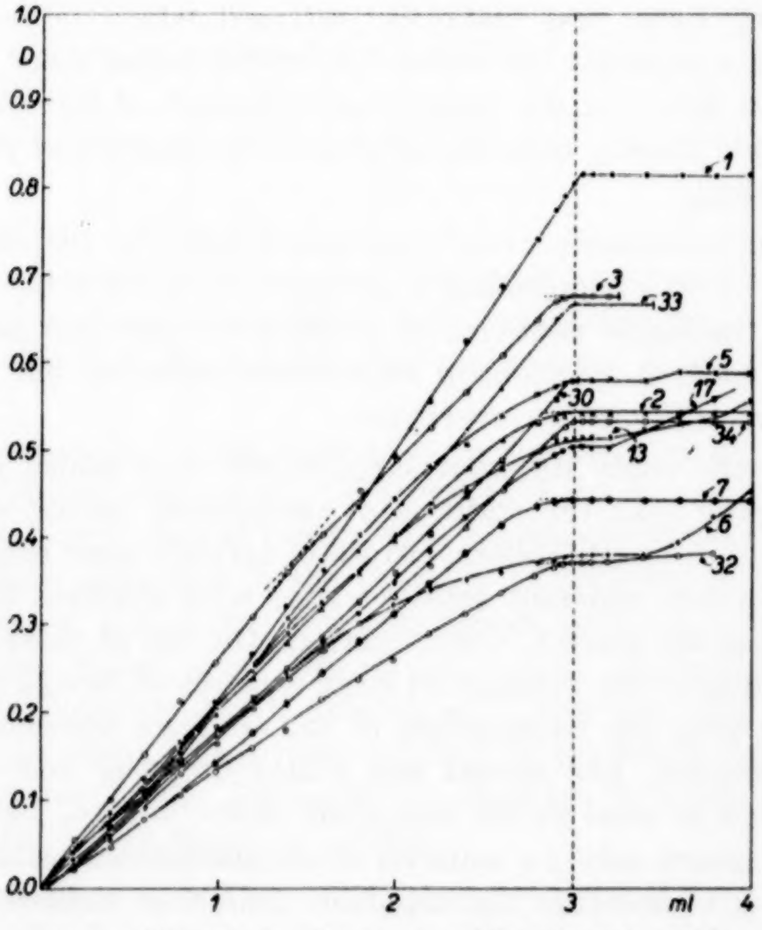


Fig. 1. Titrations of copper with rubeanic acid.

in alcohol and brought to the necessary concentration. The dilute solution was renewed every 2-3 days whilst the stock solution lasted for more than a month. No changes in the titer were noticed. All the other salts used were either analytical or chemically pure reagents.

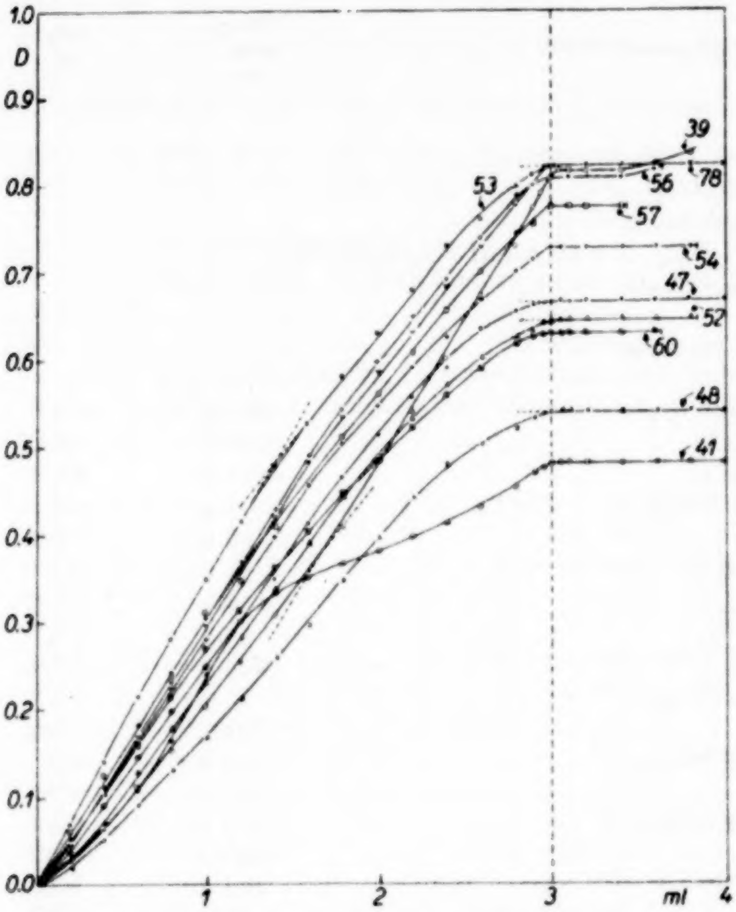


Fig. 2. Titrations of copper with rubeanic acid

Results

Tables I-III and Figs. 1 and 2 present a selection of experiments which were carried out in acid, neutral and ammoniacal solution in the presence as well as in the absence of complexing agents and foreign metals. The same numeration is used in the tables and in the figures.

EXPERIMENTAL

Experiments in neutral solution

In pure aqueous solution (expt. 38) no precipitate was obtained and the density rose after the theoretical end-point had been reached. When NH_4NO_3 was present (expt. 52) a black precipitate was obtained but the density dropped suddenly after the theoretical end-point of the titration. The drop occurred exactly at the calculated end-point.

Experiments in acid solution

In very dilute nitric acid (expt. 40) a clear green solution was obtained. The titration time was rather long. The end-point was obtained at the calculated end-point and the maximum density was high. When *nitric acid* was present in somewhat higher concentration ($0.005N$-$0.025N$) the titration became impossible (expt. 42).

Although the results with *hydrochloric acid* were different (expts. 43-44) they were also unsatisfactory.

In the presence of $0.005M$ *phosphoric acid* (expt. 45) the titration lasted longer but the maximum density value obtained was high and the error was zero. When an $0.05M$ phosphoric acid solution (expt. 46) was used the titration proceeded very slowly and took too long to reach completion.

In the presence of $0.005M$ *citric* (expt. 47) or $0.005M$ *tartaric acids* (expt. 48) the titration went smoothly, and the titration time was normal. A black precipitate was formed during the

TABL

Composition: 4 ml 0.001M Cu$(NO_3)_2$ + 4 ml M CH_3COOH + *a* ml supplements + (12-*a*) ml H_2O + x
0.00133M rubeanic acid.

Expt. number	*Supplements*	*Foreign metal mg*	*Cu %*	*x ml found*	*Initial prepn. at ml*
1	12 ml H_2O			3.0	
2	4 ml M NH_4NO_3			3.0 *i**	0.0
3	4 ,, ,, Na-acetate			3.0 *i*	0.0
4	4 ,, ,, NH_4NO_3 + 2 ml 0.1M Na_2H_2EDTA			∞	
5	1 ,, ,, Na_3-citrate			3.0	0.0
6	5 ,, ,, ,,			3.0	0.0
7	1 ,, ,, K_2-tartrate			3.0	0.0
8	5 ,, ,, ,,				
9	5 ,, ,, $Ca(NO_3)_2$	200.4	0.1	3.0 *c**	0.0
10	5 ,, ,, $BaCl_2$	686.8	0.04	3.0 *c*	0.0
11	5 ,, ,, $MgCl_2$	121.6	0.2	2.98 *c*	0.0
12	1 ,, ,, $Zn(NO_3)_2$	65.4	0.4	3.0 *i*	0.0
13	5 ,, ,, ,,	326.9	0.08	3.0 *i*	0.0
14	1 ,, ,, $MnCl_2$	54.9	0.5	3.0 *c*	0.0
15	5 ,, ,, ,,	274.7	0.09	3.0 *c*	0.0
16	1 ,, ,, $NiCl_2$	58.7	0.4	3.0 *i*	0.0
17	5 ,, ,, ,,	293.3	0.09	3.0 *i*	0.0
18	1 ,, ,, $Co(NO_3)_2$	58.9	0.4	3.0 *c*	0.0
19	5 ,, ,, ,,	294.7	0.09	3.0 *c* △*	0.0
20	1 ,, ,, $Cd(NO_3)_2$	112.4	0.2	3.0 *i*	0.0
21	5 ,, ,, ,,	562.1	0.05	3.0 *c*	0.0
22	1 ,, ,, $Pb(NO_3)_2$	207.2	0.12	3.0 *c*	0.0
23	5 ,, ,, ,,	1036.1	0.02	3.0 *i*	0.0
24	1 ,, ,, $Tl(NO_3)$	204.4	0.12	2.98	0.0
25	1 ,, ,, $AlCl_3$	27.0	0.9	3.0 *i*	0.0
26	5 ,, ,, ,,	134.9	0.2	3.0 *i*	0.0
27	1 ,, ,, $Cr(NO_3)_3$	52.0	0.5	2.98 *i* △	0.0
28	1 ,, ,, $Fe(NO_3)_3$	55.9	0.45	∞*	
29	1 ,, ,, $AlCl_3$ + 4 ml M Na-acetate	27.0	0.9	3.1	0.0
30	3 ,, ,, $AlCl_3$ + 4 ml M Na-acetate	81.0	0.3	3.0	0.0
31	1 ,, ,, $Cr(NO_3)_3$ + 4 ml M Na-acetate	52.0	0.5	3.0 *i* △	0.0
32	3 ,, ,, ,, + 5 ml 2M ,,	156.0	0.17	3.0 *c* △	0.0
33	1 ,, ,, $FeCl_3$ + 4 ml M ,,	55.9	0.45	3.0 *c* △	0.0
34	3 ,, ,, ,, + 5 ml 2M ,,	167.0	0.15	3.0 *i* △	0.0
35	1 ,, ,, $UO_2(NO_3)_2$	238.1	0.11	3.0 *i*	0.0
36	2.5 ,, ,, ,,				
37	1 ,, ,, $Th(NO_3)_4$	232.1	0.11	∞	2.0

* *i* = intersection point; *c* = contact point; △ = without filter;

titration. Theoretical results were obtained. In both cases a horizontal maximum density line was obtained.

In contrast to the results with citric and tartaric acid, clear green solutions were obtained in the presence of *acetic acid* (expts. 1 and 39). The maximum density values were high and the first maximum density point was obtained at the theoretical end-point. The concentration of acetic acid which was relatively high had no influence on the results. When the acid solution contained, in addition, large excesses of *ammonium nitrate,* the first maximum density point occurred at the theoretical end-point, and a black precipitate was obtained, but the horizontal maximum density line was lower (expt. 2). Similar results were obtained in the presence of an excess of *sodium acetate* (expt. 3) at pH $\sim$ 4.7.

Using *ethylenediaminetetraacetate* at pH $\sim$ 4.7 (expt. 4) neither colour nor precipitate appeared and no reaction occurred (expt. 5).

When *sodium citrate* was present in 0.05M (expt. 5) the titration ran smoothly, a black precipitate appeared and the error was zero. A horizontal maximum density line was obtained. When

ontent: 0.25416 mg copper in 20 ml (= $2 \cdot 10^{-4} M$).
emp. = 20° C. Filter: Corning (Fisher) green No. 4010.

Maximum density value	*Approx. titration time in min*	*Error %*	*Remarks*
0.82	9	0.0	deep green solution, precipitation after several hours.
0.55	7	0.0	horiz. max. density line till 3.4 ml, then density rises, black ppt.
0.68	3	0.0	,, ,, ,, ,, ,, 3.4 ml, then density drops, black ppt.
0.02	18		no precipitation.
0.58	7	0.0	horiz. max. density line throughout, black ppt.
0.38	50	0.0	,, ,, ,, ,, till 3.5 ml, ,, ,,
0.44	6	0.0	,, ,, ,, ,, throughout, ,, ,,
			a separation of K_2-tartrate during the titration.
0.53	7	0.0	horiz. max. density line throughout, black ppt.
0.54	7	0.0	,, ,, ,, ,, ,, ,, ,,
0.50	8	0.06	,, ,, ,, ,, ,, ,, ,,
0.53	7	0.0	,, ,, ,, ,, till 3.5 ml, then rise.
0.51	10	0.0	,, ,, ,, ,, ,, 3.5 ml, ,, ,,
0.57	6	0.0	,, ,, ,, ,, throughout, black ppt.
0.54	7	0.0	,, ,, ,, ,, ,, ,, ,,
0.55	7	0.0	,, ,, ,, ,, ,,
0.51	11	0.0	,, ,, ,, ,, till 3.5 ml, then rise.
0.51	8	0.0	,, ,, ,, ,, ,, 3.6 ml, ,, ,,
0.49	10	0.0	,, ,, ,, ,, ,, 3.5 ml, ,, ,, black ppt.
0.53	7	0.0	,, ,, ,, ,, ,, 3.5 ml, then small rise, black ppt.
0.51	11	0.0	,, ,, ,, ,, ,, 3.5 ml, ,, ,, ,, ,, ,,
0.49	12	0.0	,, ,, ,, ,, ,, 3.5 ml, then small rise.
0.46	27	0.0	,, ,, ,, ,, ,, 3.5 ml, ,, ,, ,,
0.61	7		,, ,, ,, ,, ,, 3.5 ml, ,, ,, ,,
0.54	10	0.0	,, ,, ,, ,, ,, 3.5 ml, ,, ,, ,,
0.51	14	0.0	,, ,, ,, ,, ,, 3.5 ml, ,, ,, ,,
0.45	8	0.06	,, ,, ,, ,, throughout.
0.04	15		clear brown solution.
0.71	4		just after the maximum point, a sharp drop, fine ppt.
0.58	6	0.0	,, ,, ,, ,, ,, ,, ,, ,, ,,
0.58	4	0.0	horiz. max. density line throughout, fine ppt.
0.37	4	0.0	,, ,, ,, ,, ,, ,, ,,
0.66	3	0.0	,, ,, ,, ,, ,, ,, ,,
0.53	4	0.0	,, ,, ,, ,, ,, black ppt.
0.49	12	0.0	,, ,, ,, ,, ,,
			no clear end-point.
0.40			a fine grey ppt.

= density increases beyond the calculated end-point.

this substance was present in a five times higher concentration (expt. 6) the titration took about seven times longer and the maximum density value obtained was much lower.

In the more dilute *sodium tartrate* solutions the results were similar to the corresponding results with citrates (expt. 7).

Experiments with complexing agents in neutral solutions

In the presence of 0.005*M* *potassium cyanide* no reaction whatever occurred for copper with rubeanic acid (expt. 51).

In *sodium citrate* solution a black precipitate appeared. The maximum density line rose slowly after the maximum (expt. 49). Vague results were obtained in tartrate solution.

Experiments in ammoniacal solutions

In the presence of large excess of *ammonia*, but in the absence of additional electrolytes (expts. 59 and 60) a black precipitate appeared. The end-point of the titration was obtained at the

TABLE

Composition: 4 ml 0.001 M $Cu(NO_3)_2$ + *a* ml supplements + (16-*a*) ml H_2O + *x* ml 0.00133M rubeanic ac

Expt. number	*Supplements*	*x ml found*	*Initia prepn. at ml*
38	16 ml H_2O	∼3.0	
39	1 ml M CH_3COOH	3.0	
40	1 ,, 0.05M HNO_3	3.0	0.2
41	1 ,, 0.1M HNO_3	3.0	0.0
42	5 ,, 0.1 ,, ,,		
43	1 ,, 0.1 ,, HCl		
44	5 ,, 0.1 ,, ,,	∼2.6	2.2
45	1 ,, 0.1 ,, H_3PO_4	3.0	0.0
46	1 ,, M ,,		
47	1 ,, 0.1M citric acid	3.0	0.0
48	1 ,, 0.1 ,, tartaric acid	3.0	0.0
49	1 ,, M Na_3-citrate	3.0	0.0
50	1 ,, ,, K_2-tartrate	∼2.5	
51	1 ,, 0.1M KCN		
52	2 ,, M NH_4NO_3	3.0	0.0
53	2 ,, 2M ,, + 2 ml 2M NH_3		0.0
54	2 ,, M ,, + 2 ,, M ,, + 2 ml M Na_3-citrate	3.0	0.0
55	2 ,, ,, ,, + 2 ,, ,, ,, + 2 ,, ,, K_2-tartrate	3.1	0.0
56	— 1 ,, conc. NH_3 + 5 ml M Na_3-citrate	3.0	0.0
57	— 1 ,, ,, ,, + 5 ,, ,, K_2-tartrate	3.0	0.0
58	5 ml 2M NH_4NO_3 + 1 ,, ,, ,, —	3.0	0.0
59	— 2 ,, 2M ,, —	3.0	0.0
60	— 1 ,, conc. NH_3 —	3.0	0.0
61	10 ml alcohol + 1 ,, ,, ,, —	2.9	0.0

calculated theoretical end-point and was marked by a sudden drop of the density value. The concentration of the ammonia had no influence on the results. The titrations had to be carried out extremely quickly because of the drop in the density values during the readings of the galvanometer. A titration lasted 3 minutes only. A similar experiment was carried out in 50% alcoholic solution (expt. 61) but the disturbances were unchanged.

Similar results were obtained (expt. 58) in the presence of large excesses of *ammonium nitrate*.

Experiments in ammoniacal citrate or tartrate solutions

Table II, expts. 54-57 give the results of these experiments. In the absence of ammonium nitrate (expts. 56-57) with both citrate and tartrate the titration proceeded extremely quickly and was finished after 3 minutes. The error was zero. A horizontal maximum density line which lay at the theoretical end-point was obtained after the first maximum point was reached. The sensitivity was high. A similar result was obtained in the presence of an excess of ammonium nitrate with citrate (expt. 54). In the case of tartrate the density drops at the approximate end-point.

Experiments in the presence of excesses of foreign metals

Tables I and III, and Figs. 1 and 2, present the compositions of the experiments and the results obtained.

In acetic acid solution. Almost all the titrations were carried out in the absence of complexing agents. This was the case in concentrated solutions of foreign salts in which the copper made up $\gtrsim$ 0.1% of the total metal content. Almost without exception, theoretical results were obtained in all cases. The maximum density values obtained were almost of the same order of magnitude. This seems to show that the presence of the foreign metal had no influence on the titration of copper. After the *first* maximum density point, a *horizontal* density line was obtained in all cases and this was sufficiently long for a safe titration and an easy determination of the end-point. In all cases a fine black precipitate was obtained during the titration. In no case, in the presence ntent: 0.25416 mg copper in 20 ml (= $2 \cdot 10^{-4} M$). Temp. = 20° C. Filter: Corning (Fisher) green No. 4010.

aximum density value	*Approx. titration time in min*	*Error %*	*Remarks*
0.90	10		clear green solution, density rises beyond the maximum.
0.82	5	0.0	,, ,, ,, horiz. max. density line.
0.93	24	0.0	,, ,, ,,
0.48	30	0.0	horizontal maximum density line.
0.0			no precipitation occurs after long standing.
0.0	15		precipitation occurs only after long standing.
0.52	13		after the maximum, sudden drop.
0.95	19	0.0	horizontal maximum density line, fine turbidity.
			titration very slow.
0.66	7	0.0	horizontal maximum density line, black ppt.
0.54	11	0.0	,, ,, ,, ,, ,, ,,
0.61	10	0.0	maximum density line rises slowly, black ppt.
0.0			
0.65	5	0.0	black precipitate, density drops immediately after maximum.
0.83	5		,, ,, ,, ,, ,, ,, ,,
0.72	3	0.0	horizontal maximum density line.
0.73	3	+3.3	density drops after the maximum.
0.81	3	0.0	horiz. max. density line till 3.6 ml, then drop, black ppt.
0.77	3	0.0	,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,,
0.80	3	0.0	density drops suddenly after maximum, black ppt.
0.78	3	0.0	,, ,, ,, ,, ,, ,, ,,
0.65	3	0.0	,, ,, ,, ,, ,, ,, ,,
0.88	3	−3.3	,, ,, ,, ,, ,, ,, ,,

of foreign bivalent cations, was a complexing agent necessary. Only in the presence of excesses of trivalent cations, especially in the presence of iron, was a large excess of *sodium acetate* needed to produce a successful titration. The titration time was generally low, less than 10 minutes. With bivalent cations the time was longer in the more concentrated solutions of the foreign salts.

The results obtained in the presence of large excesses of *coloured cations* such as *nickel* or *cobalt* (expts. 16-19) were very favourable. In both cases (expts. 17 and 19) the metals made up 99 9% of the total metal content. *Traces of copper can therefore be determined heterometrically in nickel or cobalt.* The percentage of copper in these metals can probably be reduced still further. The *magnesium* (expt. 11) made up 99.8% but there is no doubt that a much higher content could be present and yet traces of copper could still be determined in magnesium.

Only in the case of *lead* (expts. 22 and 23) was the titration time much longer with the higher percentage of lead. But in spite of this, the maximum density values remained the same.

As to the titrations of copper in the presence of *aluminium* they were best carried out in the absence of sodium acetate (expts. 25, 26, 29 and 30). The aluminium made up 99.8% but as the density value (expt. 26) was not at all influenced by the amount of aluminium in solution, there is no doubt that this metal could be present in a much higher percentage. *Traces of copper therefore, can be very successfully determined in aluminium alloys.*

In the presence of *chromium* or *iron* no green filter was used as it reduced the density and made the determination more difficult. With iron(III) the titrations could be carried out only in the presence excess of sodium acetate (expts. 33 and 34). In the absence of sodium acetate (expt. 28) no end-point was obtained and the density rose after the end-point. The iron made up 99.85% (expt. 34).

Copper, constituting $\sim$ 0.1% was determined without any difficulty in *Ca, Ba, Zn, Mn, Cd and Tl.* In *uranium* the copper made up 0.1%.

When certain cations, *viz.* Hg, Ag, Sb and Bi, were present in excess, copper could not be determined in acid solution.

TABLE

Composition: 4 ml 0.001 M $Cu(NO_3)_2$ + a ml supplements + (16-a) ml H_2O + x ml 0.00133 M rubeanic a

Expt. number	*Supplements*	*Cu %*	*x ml found*
62	1 ml M $Zn(NO_3)_2$ + 5 ml M Na_3-citrate	0.4	∞*
63	1 ,, ,, $NiCl_2$ + 5 ,, ,, ,,	0.4	
64	1 ,, ,, $Co(NO_3)_2$ + 5 ,, ,, ,,	0.4	
65	1 ,, ,, $Cd(NO_3)_2$ + 5 ,, ,, ,,	0.2	
66	1 ,, ,, $Zn(NO_3)_2$ + 5 ,, ,, ,, + 1 ml NH_3 conc.	0.4	
67	1 ,, ,, $MnCl_2$ + 5 ,, ,, ,, + 1 ,, ,, ,,	0.5	3.0 *i**
68	3 ,, ,, ,, + 5 ,, ,, ,, + 1 ,, ,, ,,	0.17	3.0 *i*
69	1 ,, ,, $NiCl_2$ + 5 ,, ,, ,, + 1 ,, ,, ,,	0.4	
70	1 ,, ,, $Co(NO_3)_2$ + 5 ,, ,, ,, + 1 ,, ,, ,,	0.4	△*
71	1 ,, ,, $Cd(NO_3)_2$ + 5 ,, ,, ,, + 1 ,, ,, ,,	0.2	
72	1 ,, ,, $Pb(NO_3)_2$ + 5 ,, ,, ,, + 1 ,, ,, ,,	0.12	
73	1 ,, ,, $AlCl_3$ + 5 ,, ,, ,, + 1 ,, ,, ,,	0.9	3.0 *i*
74	3 ,, ,, ,, + 5 ,, ,, ,, + 1 ,, ,, ,,		
75	1 ,, ,, $FeCl_3$ + 5 ,, ,, ,, + 1 ,, ,, ,,	0.45	3.0 *i*
76	3 ,, ,, ,, + 5 ,, ,, ,, + 1 ,, ,, ,,	0.15	
77	1 ,, ,, $Cr(NO_3)_3$ + 5 ,, ,, ,, + 1 ,, ,, ,,	0.5	
78	1 ,, ,, $Bi(NO_3)_3$ (HNO_3) + 5 ml M Na_3-citrate + 2 ml NH_3 conc.	0.12	3.0
79	0.8 ,, ,, $SbCl_3$ (HCl) + 5 ,, ,, ,, + 2 ,, ,, ,,	0.26	3.0
80	1 ,, ,, $Zn(NO_3)_2$ + 5 ml M K_2-tartrate + 1 ml NH_3 conc.	0.4	
81	1 ,, ,, $MnCl_2$ + 5 ,, ,, ,, + 1 ,, ,, ,,	0.5	3.0 *i*
82	3 ,, ,, ,, + 5 ,, ,, ,, + 1 ,, ,, ,,	0.17	
83	1 ,, ,, $NiCl_2$ + 5 ,, ,, ,, + 1 ,, ,, ,,	0.4	
84	1 ,, ,, $Co(NO_3)_2$ + 5 ,, ,, ,, + 1 ,, ,, ,,	0.4	△
85	1 ,, ,, $Cd(NO_3)_2$ + 5 ,, ,, ,, + 1 ,, ,, ,,	0.2	
86	1 ,, ,, $Pb(NO_3)_2$ + 5 ,, ,, ,, + 1 ,, ,, ,,	0.12	3.0 *c**
87	3 ,, ,, ,, + 5 ,, ,, ,, + 1 ,, ,, ,,	0.04	
88	1 ,, ,, $FeCl_3$ + 5 ,, ,, ,, + 1 ,, ,, ,,	0.45	3.0 *i*
89	3 ,, ,, ,, + 5 ,, ,, ,, + 1 ,, ,, ,,	0.15	
90	1 ,, ,, $SbCl_3$(HCl) + 5 ,, ,, ,, + 2 ,, ,, ,,	0.21	3.0

* *i* = intersection point; *c* = contact point; △ = without filter;

Experiments in neutral or ammoniacal solutions

The results are compiled in Table III. The experiments were mostly carried out in the presence of large excesses of ammonia, in addition to a molar excess of sodium citrate or tartrate. A glance at the table shows that in very many cases no clear end-point was obtained. In most cases the density increased beyond the calculated end-point.

Only in special cases could copper be precisely determined in the presence of large excesses of foreign metals. Amongst those was, surprisingly, *manganese* (in citrate) which caused no difficulties (expts. 67 and 68) even though this metal made up 99.8%. To a certain degree (∼ 0.1% Cu) *lead* in tartrate (expt. 86) showed the same behaviour. A horizontal maximum density line was obtained and the titration time was short.

In all other cases, in excesses of *bi*valent cations, the determination of copper was unsuccessful. The results in the presence of excesses of trivalent cations stand in contrast to this. Thus the determination of *aluminium* (expt. 73) and *iron* (expt. 75) was carried out in the presence of excess citrate. The percentage of copper in these solutions was of course higher than in acetic acid milieu.

The titrations of copper in the presence of ∼ 99.8% of *antimony* (expts. 79 and 90) and *bismuth* (expt. 78) were very successful. In antimony the titration could be made either in excess of citrate or in tartrate solutions (in the latter case a sudden density drop occurred at the calculated end-point), but with bismuth the determination could be made in excesses of citrate only. *This was the only way of successfully determining copper in these metals.*

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ntent: 0.25416 mg copper in 20 ml ($= 2 \cdot 10^{-4} M$). Temp. = 20° C. Filter: Corning (Fisher) green No. 4010.

itial epn. ml	*Maximum density value*	*Approx. titration time in min*	*Error %*	*Remarks*
.0	∞0.5	18		a grey precipitate.
.0	∞0.6	15		
.0	∞0.4	23		
.0				a white precipitate.
.0	∞0.60	6		a black ,,
.0	0.73	3	0.0	horizontal maximum density line till 3.6 ml, then drop.
.0	0.73	5	0.0	,, ,, ,, ,, ,, ,, ,, ,, ,,
.0	∞0.70	7		fine precipitate.
.0	∞0.20	3		turbid.
.0	∞0.40	8		fine grey precipitate.
.0	∞0.68	6		
.0	0.79	3	0.0	horizontal maximum density line till 3.4 ml, then drop. precipitation at the beginning.
.0	0.76	4	0.0	horizontal maximum density line till 3.7 ml, then drop. precipitation at the beginning.
				,, ,, ,, ,,
.0	0.82	5	0.0	horizontal maximum density line throughout.
.0	0.63	4	0.0	,, ,, ,, ,, till 3.8 ml, then drop.
.0	∞0.50	6		black precipitate.
.0	0.76	5	0.0	horizontal maximum density line till 3.6 ml, then rise.
.0	∞0.70	8		black precipitate.
.0	∞0.75	7		fine ,,
.0	∞0.20	3		turbid.
.0	∞0.45	8		fine grey precipitate.
.0	0.70	6	0.0	horizontal maximum density line, black precipitate.
.0	∞0.80	6		
.0	0.79	3	0.0	horizontal maximum density line till 3.6 ml, then drop, black ppt.
.0	∞0.65	4		fine precipitate.
.0	0.74	3	0.0	sudden density drop after the maximum point.

= no maximum density point, density increases beyond the calculated end-point.

Method

1. *General remarks.* The two methods presented below are used in the following cases.

The *acetic acid method* has to be used in all cases where traces of Cu^{+2} are to be determined in aqueous solutions in general, in alloys or in the presence of $\gtrsim$ 99.9% of the following cations: monovalent: Tl; bivalent: Ca, Ba, Mg, Zn, Mn, Ni, Co, Cd and Pb; trivalent: Al, Cr and Fe.

The *ammoniacal method* can only be used in special cases when the acetic acid method cannot be applied successfully. This is the case when copper is analysed in solutions or in alloys which contain *antimony* or *bismuth* up to $\sim$99.8%. Traces of copper can also be determined in Mn^{+2}, Pb^{+2} as well as in Al^{+3}, Cr^{+3} or Fe^{+3}. In all these cases the analysed solution must contain a molar excess (based on the foreign metal) of alkali-citrate (or tartrate) as well as of ammonia.

2. *Titration in acetic acid solution.* 20 ml of an aqueous solution containing 4 ml M acetic acid and about 0.2 mg copper and which may contain, in addition, $\gtrsim$ 99.9% of foreign metals, are titrated heterometrically at 20° C with $\sim$ 0.001 M rubeanic acid (dissolved in alcohol). A green filter is used in all titrations.

In the presence of ferric iron (or chromium) no filter is used and a molar excess of sodium acetate must be added in addition to the acetic acid. An "ultra rapid" method of titration is used: the readings are made each time at the maximum deflection of the galvanometer which occurs almost instantly after the dropwise addition of titrant.

The titration time is mostly less than 10 minutes and the error is generally close to zero.

3. *Titration in ammoniacal solution.* Alloys or other compounds which contain traces of copper in bismuth and antimony ($\gtrsim$ 99.8%) or traces of copper in Fe, Cr, Al, Mn or Pb are dissolved in acid.

To an amount of this aqueous solution containing about 0.2 mg copper, a few ml of concentrated ammonia are added together with excess ($\gtrsim$ 5 ml *M*) alkali citrate. Then 20 ml of the solution so obtained are titrated at 20° C heterometrically with a $\sim$ 0.001*M* rubeanic acid (dissolved in alcohol).

The dropwise addition of the rubeanic acid must be carried out almost continuously whilst making readings of the galvanometer.

The titration time is 3-6 minutes. The error is generally close to zero.

SUMMARY

About 0.2 mg copper in 20 ml aqueous acetic acid, containing in addition 99.9-99.98% of foreign mono-, bi- or trivalent metals, were determined heterometrically at 20° C with $\sim$ 0.001*M* rubeanic acid. The monovalent cation present was Tl, the bivalent cations: Ca, Ba, Mg, Zn, Mn, Ni, Co, Cd and Pb and the trivalent cations: Fe, Cr and Al. In the presence of trivalent Sb or Bi an ammoniacal citrate or tartrate solution was used. In most cases the error was close to zero.

RÉSUMÉ

Environ 0.2 mg de cuivre peuvent être dosés par hétérométrie, dans 20 ml d'une solution aqueuse d'acide acétique, renfermant 99.9 à 99.98% de cations étrangers mono-, bi-, ou trivalents, à 20° C, au moyen d'acide rubéanique $\sim$ 0.001*M*. (Cation monovalent: Tl; cations bivalents: Ca, Ba, Mg, Zn, Mn, Ni, Co, Cd et Pb; cations trivalents: Fe, Cr, Al.) En présence d'antimoine et de bismuth trivalents, on a utilisé une solution ammoniacale de citrate ou de tartrate. Dans la plupart des cas, les résultats sont presque théoriques.

ZUSAMMENFASSUNG

Ungefähr 0.2 mg Kupfer in 20 ml verdünnt essigsaurer Lösung welche ausserdem 99.9-99.98% einwertige, zweiwertige oder dreiwertige Fremdmetalle enthielt, wurden bei 20° C mit $\sim$ 0.001*M* Rubeansäure heterometrisch bestimmt. Das einwertige Kation war: Tl, die zweiwertigen Kationen: Ca, Ba, Mg, Zn, Mn, Ni, Co, Cd und Pb und die dreiwertigen Kationen: Fe, Cr und Al. In Gegenwart von dreiwertigem Sb oder Bi wurde eine ammoniakalische Citrat- oder Tartratlösung verwendet. In den meisten Fällen war der Fehler nahezu gleich null.

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THE DETERMINATION OF ORGANIC BASES WITH HEXANITRODIPHENYLAMINE

PART I. GENERAL STUDY

by

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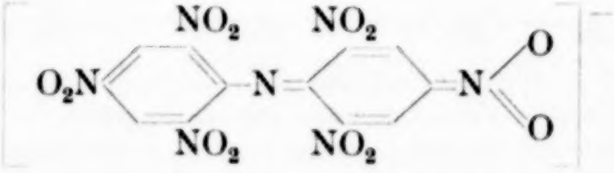
Aromatic nitro compounds produce orange or red colours in alkaline solution. This generally known phenomenon is employed for the determination of these compounds[1].

2,2′,4,4′,6,6′-Hexanitrodiphenylamine (= HNDA), also known as dipicrylamine, like other aromatic nitro compounds exists as two tautomers, the yellow baso-form and the red aci-form[2]. The yellow form of HNDA is the molecular[3] form of a strong acid which is stable in solvents of low dielectric constant, as well as in other solvents in the presence of strong mineral acids. The red form is the anion of the dissociated acid, existing in solvents of high dielectric constant as well as in solvents of low dielectric constant even when quite weak proton acceptors are present.

HNDA is widely employed as a precipitant for potassium. The literature deals almost exclusively with different analytical methods for the determination of potassium employing the reagent[4].

It was observed that a yellow dioxane solution of HNDA turns orange or red on the addition of organic bases (they acting as proton-acceptors) the intensity varying with the base added.

The reaction between HNDA, a strong acid, and an organic base, produces the anion of the HNDA *iso*-nitro acid[3]. The colour of this ion is derived from the system of conjugated double bonds:



The colours formed were found to be stable under the experimental conditions tried, and provided a basis for the colorimetric determination of these bases. This paper deals with the reactions of various organic bases with HNDA and shows the feasibility of using the colour changes for a colorimetric determination. A second paper will deal with a precise colorimetric determination of pyridine (with special emphasis on the determination of traces of pyridine in ethyl alcohol) using HNDA.

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EXPERIMENTAL

Reagents

The HNDA was an Eastman Kodak reagent for laboratory use. The 3,3′-diaminodipropylamine, *n*-butylamine, *iso*-butylamine, *tert.*-butylamine, di-*n*-butylamine, 2,4,6-trimethylpyridine and allylamine used were Eastman Kodak (white label) reagents; the 1,2-propanediamine (90%), tri-*n*-butylamine, N-*iso*-propyl-1,3-propanediamine, 1,1,3,3-tetramethylbutylamine, 2-ethylhexylamine and 2,2′-diethyldihexylamine used were Eastman Kodak practical (yellow label) reagents; the α- and β-picoline, ethylenediamine, trimethylamine (33% w/v alcoholic solution), pyridine (redistilled), and dioxane (purified) used were B.D.H. reagents. The aniline was a J. T. Baker's c.p. product; and the benzylamine, N-ethylpiperidine, phenylhydrazine, diethylaniline, triethylamine and piperidine were supplied by L. Light & Co. None of the compounds was further purified before use.

A 0.01 *M* solution of HNDA was prepared by dissolving the yellow crystals in dioxan. Fresh solutions were always used as they are unstable, turning appreciably orange in 24 hours and consequently becoming unsuitable for measurement.

Apparatus and procedure.

For the spectrophotometric measurements a Beckman DU spectrophotometer was used, employing 10 mm Beckman glass cells.

The experiments were carried out by adding 17 ml of dioxane and 1 ml of various liquid organic bases to 2 ml of a 0.01 *M* solution of HNDA in dioxane so that in each case the solutions contained 95% dioxane and 5% of the organic base used.

RESULTS AND DISCUSSION

By the addition of 5% of the liquid organic base to the yellow dioxane solution of HNDA a red colour was obtained. Spectrophotometric measurements of these red solutions were made in order to obtain absorption curves in the visible range of the spectra. The shifts of the absorption curve of the yellow dioxane solution caused by the addition of the organic bases are presented in Table I. Some of the curves obtained are shown in Fig. 1.

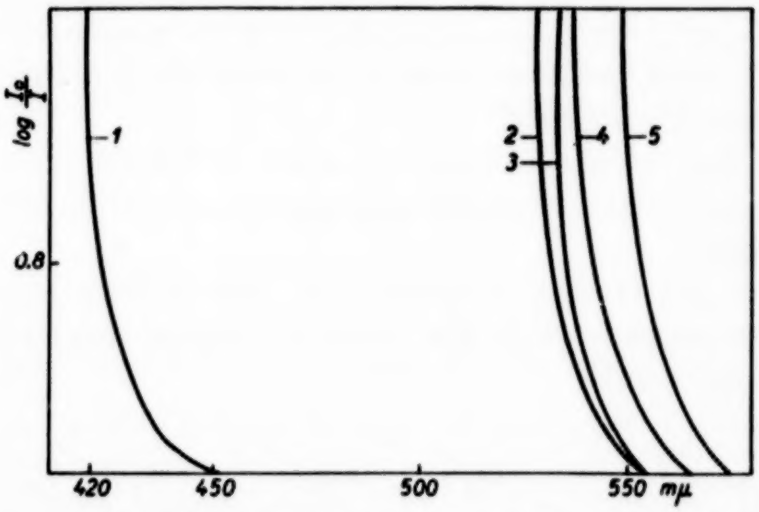

Fig. 1. Absorption curves of HNDA solutions in presence of various liquid organic bases
1) 2 ml 0.01 *M* HNDA + 18 ml dioxane (for comparison)
2) 2 ml 0.01 *M* HNDA + 17 ml dioxane + 1 ml 1,2-propanediamine
3) 2 ml 0.01 *M* HNDA + 17 ml dioxane + 1 ml phenylhydrazine
4) 2 ml 0.01 *M* HNDA + 17 ml dioxane + 1 ml *n*-butylamine
5) 2 ml 0.01 *M* HNDA + 17 ml dioxane + 1 ml 2,2′-diethyldihexylamine

As seen, the shifts caused are more than sufficiently large to provide a basis for colorimetric determination of these bases by the HNDA reagent. With all bases investigated, except aniline, the shift of the absorption curve to higher wavelengths differed by 103 to 130 mμ, from the value for HNDA in dioxane which was 424 mμ.

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TABLE I

GENERAL COMPOSITION OF THE EXPERIMENTS:
2 ml 0.01*M* HNDA IN DIOXANE + 17 ml DIOXANE + *x* ml BASE

No.	*Organic base*	*Formula*	K_b[(a)]	*Wavelength in mμ*[(b)]	*Longitude of the shift in mμ*
1.	Ethylenediamine	$C_2H_8N_2$	$8.5 \cdot 10^{-5}$	538	114
2.	Trimethylamine	C_3H_9N	$7.4 \cdot 10^{-5}$	546	122
3.	Triethylamine	$C_6H_{15}N$	$6.4 \cdot 10^{-4}$	545	121
4.	Allylamine	C_3H_7N	$5.7 \cdot 10^{-5}$	538	114
5.	*n*-Butylamine	$C_4H_{11}N$	$4.1 \cdot 10^{-4}$	542	118
6.	*iso*-Butylamine	$C_4H_{11}N$	$3.1 \cdot 10^{-4}$	542	118
7.	*tert.*-Butylamine	$C_4H_{11}N$	$2.8 \cdot 10^{-4}$	544	120
8.	Di-*n*-butylamine	$C_8H_{19}N$	$2.1 \cdot 10^{-3}$	546	122
9.	Tri-*n*-butylamine	$C_{12}H_{27}N$		546	122
10.	1,1,3,3-Tetramethylbutylamine	$C_8H_{19}N$		550	126
11.	3,3′-Diaminodipropylamine	$C_6H_{17}N_3$		532	108
12.	1,2-Propanediamine	$C_3H_{10}N_2$		532	108
13.	N-*iso*-Propyl-1,3-propanediamine	$C_6H_{16}N_2$		532	108
14.	2-Ethylhexylamine	$C_8H_{19}N$		543	119
15.	2,2′-Diethyldihexylamine	$C_{16}H_{35}N$		554	130
16.	Benzylamine	C_7H_9N	$2.4 \cdot 10^{-5}$	543	119
17.	Phenylhydrazine	C_6H_8N	$1.6 \cdot 10^{-9}$	536	112
18.	Aniline	C_6H_7N	$4.6 \cdot 10^{-10}$	456	32
19.	Diethylaniline	$C_{10}H_{15}N$	$2.7 \cdot 10^{-8}$	527	103
20.	Pyridine	C_5H_5N	$2.3 \cdot 10^{-9}$	542	118
21.	α-Picoline	C_6H_7N	$3.0 \cdot 10^{-8}$	538	114
22.	β-Picoline	C_6H_7N	$1.0 \cdot 10^{-8}$	538	114
23.	2,4,6-Trimethylpyridine	$C_8H_{11}N$	$2.1 \cdot 10^{-7}$	536	112
24.	Piperidine	$C_5H_{11}N$	$1.6 \cdot 10^{-3}$	548	124
25.	N-Ethyl-piperidine	$C_7H_{15}N$	$8.2 \cdot 10^{-4}$	544	120
	Dioxane(c)			424	

(a) Values from the "Landolt-Bornstein physikalisch-chemische Tabellen"
(b) Wavelength where the absorbancy value is equal to 0.800
(c) 2 ml 0.01*M* HNDA in dioxane + 18 ml dioxane (for comparison)

A minimum shift of the absorption curve amounting to only 32 mμ was obtained with aniline. This relatively small shift of the absorption curve of HNDA caused by aniline, is probably best explained by the weak acidity of aniline as a base.

In the experiments carried out the amount of organic base present was approximately 50 times greater than the amount needed for stoichiometric neutralization of the HNDA as acid (the final concentration of HNDA in 20 ml volume was $10^{-3}M$ and of the bases approximately $5 \cdot 10^{-2}M$). At such a ratio of acid to base, a complete ionization of the HNDA was obtained (except with aniline), which produced a deep red colour in the solution. In a further set of experiments the molar ratio of the base to the acid was 1:1. In all cases an orange colour was obtained. In experiments where a more concentrated solution of HNDA in dioxane (0.1*M*) was used, an appreciable orange colour was obtained, even in cases where smaller amounts of organic bases were used, the concentration varying from 10^{-6} to $10^{-4}M$. These values indicate the useful range of concentration at which quantitative colorimetric measurements can be made, and the details will be shown in the further paper.

Experiments were carried out with almost all the organic bases mentioned in

Table I, in order to check the validity of Beer's law. In all cases investigated it was found that solutions containing less than 10 mg of base in 10 ml of total volume obeyed Beer's law. In some cases the law was found to be invalid with quantities smaller than 0.5 mg, and in a few cases the maximum amounts obeying Beer's law were found to be even higher than 10 mg in 10 ml volume.

Several solvents, other than dioxane, were tried and those with a low dielectric constant, such as chloroform, carbon tetrachloride, benzene and ethyl ether were found to be suitable as solvents for the HNDA reagent (the solution being yellow) and as mediums for the determination — presuming of course that the organic bases were soluble in them. In contrast, organic solvents with intermediate or high dielectric constants like acetone, methyl and ethyl alcohol interfere with the sharpness of the determination when present in larger quantities, since the dissolved HNDA is itself orange in these solvents. Water, as a solvent of the highest dielectric constant of these mentioned, is practically unusable, reacting with HNDA and causing total ionization of the acid.

The reaction which is the basis for the method suggested is very sensitive but not specific, being unable to provide for the determination of a weak organic base when any other base, organic or inorganic, is present.

ACKNOWLEDGEMENT

The author wishes to thank Mr. J. M. E. Goldschmidt for his interest in this work.

SUMMARY

A yellow solution of hexanitrodiphenylamine produces orange or red colour with organic bases. The different intensities of the orange and red colours are sufficiently characteristic to permit the quantitative determination of several organic bases.

RÉSUMÉ

La solution jaune d'hexanitrodiphénylamine donne avec les bases organiques une coloration rouge ou orange. Les intensités des colorations obtenues sont suffisamment caractéristiques pour permettre un dosage de plusieurs composés organiques basiques.

ZUSAMMENFASSUNG

Die gelbe Lösung von Hexanitrodiphenylamin färbt sich bei Zugabe organischer Basen orange bis rot. Die Intensitäten der orangen und roten Färbungen sind charakteristisch und können für die quantitative Bestimmung mehrerer organischer Basen herangezogen werden.

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ESTIMATION OF THE HIGHER FATTY ACIDS C_7-C_{18}

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Fatty acids are usually estimated by titration in hot methanolic solution against potassium hydroxide using phenolphthalein as indicator. This method has several disadvantages when applied to the higher fatty acids. It is often necessary to reheat the solution of these fatty acids during the titration to prevent precipitation of the acid and the formation of a gel by the potassium salt of the acid as the solution cools. Solutions of the higher fatty acids may contain coloured substances which prevent the use of indicators; the titration may be carried out potentiometrically but because the solutions are hot and the acids relatively weak, the end-points obtained by this method are not good. Another disadvantage of the titration method is that any basic or other acidic impurity is also titratable. This condition arises during the estimation of emulsions which contain higher fatty acids and organic bases. A method which is specific for the higher fatty acids, and does not involve a titration is therefore needed.

The metallic salts of the fatty acids other than sodium and potassium are very sparingly soluble in water and are readily precipitated from solutions of their sodium and potassium soaps by addition of a solution of a metallic salt such as the metallic nitrate. The heavy metal soaps are the least soluble. This precipitation could therefore form the basis of a gravimetric method of analysis. It suffers from the disadvantage that the heavy metal soaps often show a tendency to occlude the more soluble alkali soaps.

Although in general the metallic soaps are not very soluble in organic liquids, certain of the heavy metal soaps are appreciably soluble; in particular copper and cobalt soaps dissolve readily in chloroform to give blue and red-blue solutions respectively. This paper describes a colorimetric method of estimating the higher fatty acids which is based on this fact. The method is specific to the fatty acids in the range C_7 to C_{18} and is independent of basic or other acidic impurities. The method may also be applied to coloured solutions provided the colour is not extracted from aqueous methanol by chloroform.

The absorption spectra of copper and cobalt soaps

The copper and cobalt soaps of the higher fatty acids were prepared by precipitation from the corresponding potassium soap and copper or cobalt nitrate, and were dissolved in chloroform. The absorption spectra of these solutions were found using the Unicam SP600 spectrophotometer. Typical spectra of these solutions are shown in Fig. 1. The spectra for the copper soaps showed a maximum at 675 mμ and the cobalt soap at 525 mμ. There was very little difference between the spectra of the various fatty acids investigated. These were:

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Caprylic
Capric
Lauric
Myristic
Palmitic
Stearic
Heptanoic
Nonanoic
Undecanoic
Tridecanoic

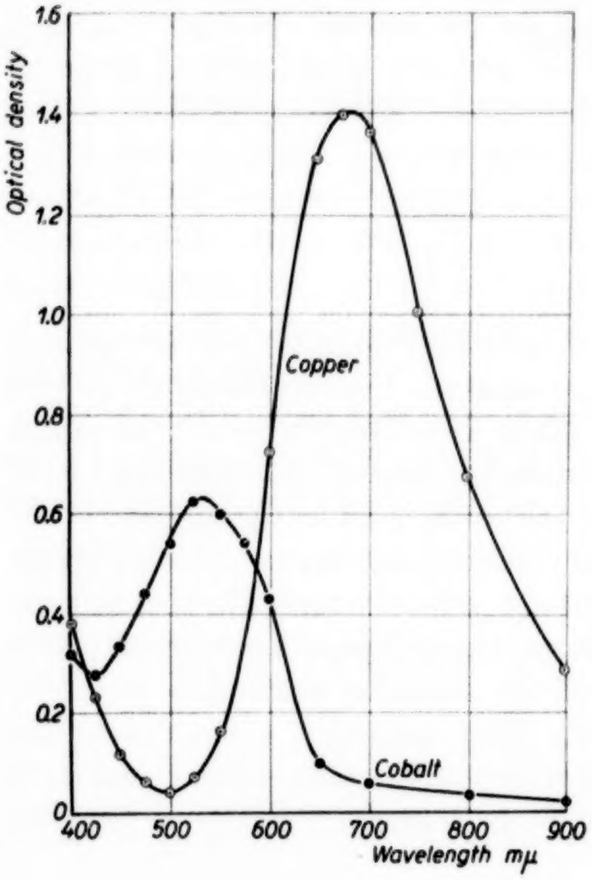

Fig. 1. Absorption spectra of copper and cobalt soaps in chloroform.

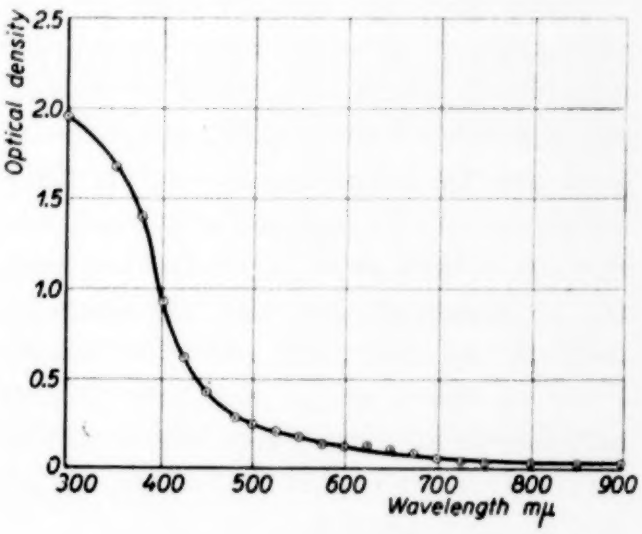

Fig. 2. Absorption spectra of cobalt salt of abietic acid in chloroform.

The lower fatty acids such as acetic, butyric, caproic gave no precipitate under the conditions of the experiment, whereas the higher fatty acids such as behenic were not sufficiently soluble even as the potassium salt for the estimation to be carried out, unless temperatures above room temperature were used. Other acids including benzoic, oxalic, succinic and malonic gave either no precipitate, or a precipitate insoluble in chloroform. This limits the method to the estimation of fatty acids in the range C_7-C_{18}. The same spectra were also obtained for the unsaturated fatty acids such as oleic. In addition abietic acid was studied as it is reported to give a bluish-red precipitate with cobalt nitrate which is soluble in chloroform[1]. When copper nitrate solution was added to a solution of the potassium salt of abietic acid a blue precipitate was formed which readily dissolved in chloroform, and had a spectrum almost identical with that of the copper soaps. Cobalt nitrate, however, gave a brownish precipitate, which although soluble in chloroform gave a spectrum with no maximum, Fig. 2.

Fig. 3 shows the spectra of aqueous solutions of copper nitrate and cobalt nitrate measured against water, and of a methanolic solution of cobalt nitrate measured against methanol. These solutions are the reagents used in the estimation of the fatty acids. Although a direct comparison cannot be made between the spectra given

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in Fig. 3 and 1 because of different solvents, there is a marked similarity between the two sets. It appears therefore that the colour which is measured in the estimation of fatty acids is due to the copper or cobalt ions, although this would not be expected in chloroform solution.

Effect of concentration on the optical density of the solutions

Beer's law was obeyed in all cases over the concentration range 0.2 to 0.04*M* for the cobalt soaps and 0.04 to 0.008*M* for the copper soaps. Below a concentration of 0.04*M* for cobalt soaps and 0.008*M* for copper soaps the solutions were too pale to be estimated accurately using 1 cm cells. Above a concentration of 0.2*M* for cobalt and 0.04*M* for copper soaps the solutions are too concentrated and the metallic soaps often precipitate out on standing (see Fig. 4).

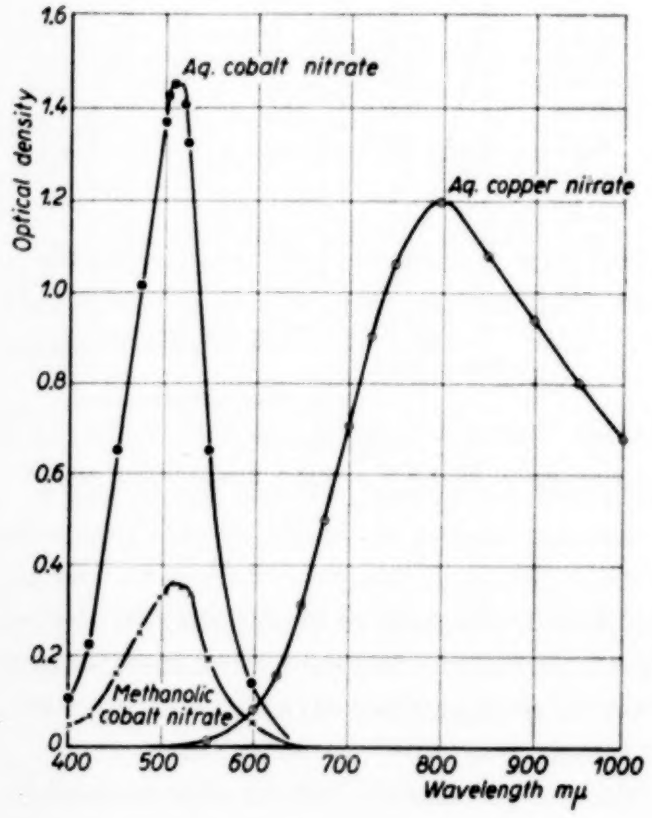

Fig. 3.
Absorption spectra of copper nitrate and cobalt nitrate in water and methanol.

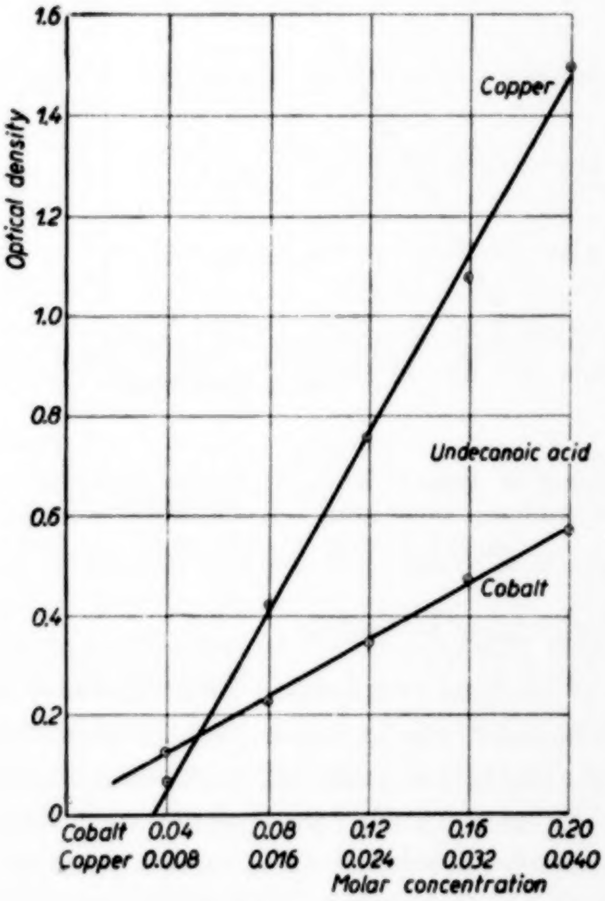

Fig. 4.
Effect of concentration on optical densities of copper and cobalt soaps in chloroform.

Although the spectrum of the cobalt salt of abietic acid showed no maximum at 525 mμ, the optical densities of solutions of varying concentrations were measured at this wavelength. A linear relationship was obtained. However, the copper salt was used for any estimations of abietic acid since its spectrum contains a good maximum, Fig. 5.

Without exception, the slopes of the optical density/concentration curves for the copper soaps were greater than those for the corresponding cobalt soaps. The copper method is therefore the more sensitive method.

The standard deviation calculated using 10 values was 0.006 for an optical density of 0.6. To find the concentration range for maximum sensitivity a RINGBOM plot (Fig. 6) was made[2]. This was linear for concentrations of 0.008 to 0.03*M* for copper salts and shows that the copper method is equally sensitive for almost the whole concentration range. A point of inflection occurs in the cobalt curve at a concentration of 0.1 *M* which is therefore the concentration for the maximum sensitivity by this method.

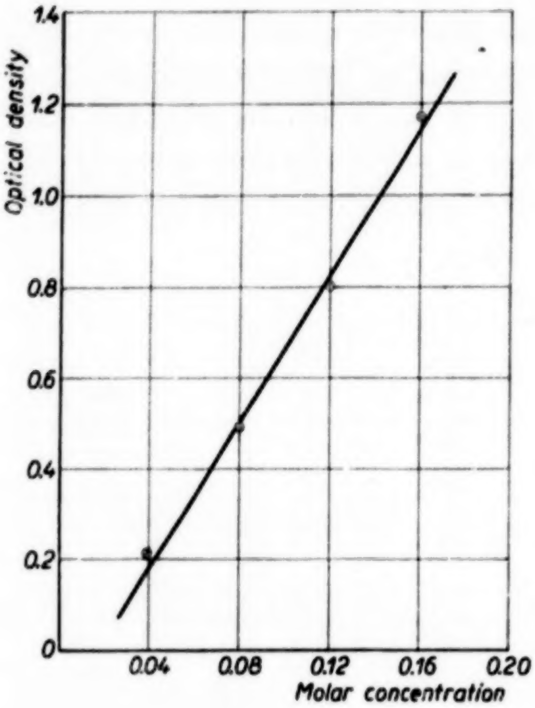

Fig. 5.
Effect of concentration on optical density of solution of cobalt salt of abietic acid in chloroform at 525 mμ.

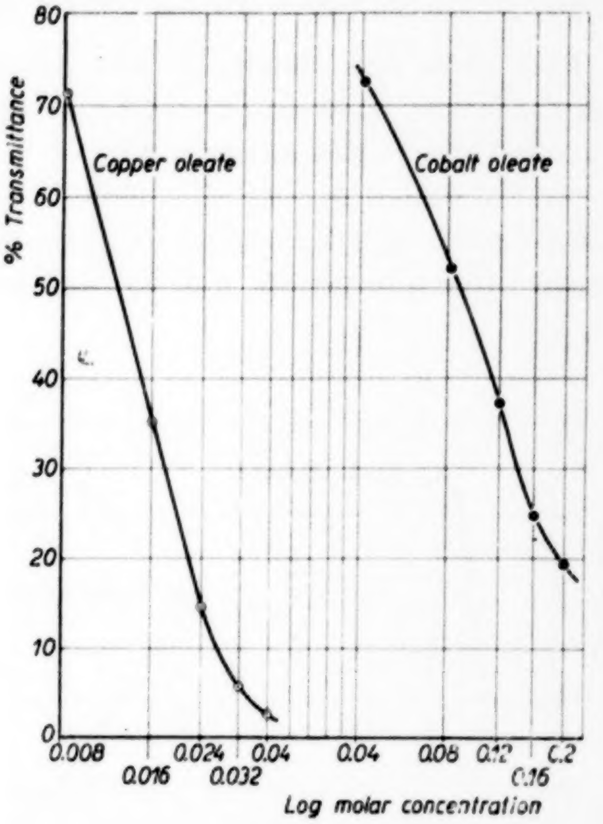

Fig. 6.
RINGBOM plot for copper and cobalt soaps.

Extraction technique

The blue precipitate formed when copper nitrate was added to a solution of the potassium soaps or the pink precipitate when cobalt nitrate was added were obtained in chloroform solution by merely extracting the suspension in water with chloroform. Filtration of the precipitate and then dissolution was unnecessary.

Since the fatty acids were usually dissolved in methanol which was miscible with chloroform, 5 to 10 ml of water was also added during the extraction to ensure separation into two layers after standing. One extraction with 10 ml of chloroform for 5 ml of acid solution was sufficient to extract all the copper or cobalt soap. A further extraction with an additional 10 ml of chloroform removed no more colour.

The cobalt soaps were also soluble in petroleum ether b.p. 100-120° C and this could be used in place of chloroform as extracting liquid. However the soaps were much less soluble in petroleum ether than in chloroform and three extractions were necessary to completely dissolve all the cobalt soaps.

The effect of pH *on the estimation*

The effect of pH on the precipitation of the copper and cobalt salts of the higher fatty acids was studied. No precipitate was formed when cobalt nitrate was added to methanolic solutions of the free acids. When copper nitrate was added, however, a precipitate was formed but to a much smaller extent than when the corresponding sodium or potassium salt was used. When the estimation of the fatty acids was carried out at various pH values, as was expected, the optical densities of the chloroform solutions of the copper and cobalt soaps increased with increase in pH until the acid had been completely neutralized. At even higher pH values, the metallic hydroxides were also precipitated, especially in the case of copper, and these precipitates interfered with the chloroform extractions. An emulsion was formed which did not readily separate into two layers.

TABLE I

THE VARIATION OF OPTICAL DENSITY WITH PH

Copper soap		*Cobalt soap*	
pH	*O.D.*	*pH*	*O.D.*
4.8	0.05	4.1	0.025
6.7	0.38	6.5	0.025
7.3	0.6	7.0	0.065
7.8	0.67	7.4	1.0
8.7	0.65	8.4	1.0
10.6	0.68	10.5	1.03
11.0	0.45	11.0	1.05

Table I illustrates the way in which the optical density varied with pH, and shows that the pH of the reacting solution was not very critical provided it was in the range 8 to 10.

The effect of sodium or potassium chloride on the estimation

Fatty acids are frequently estimated in the solution formed by the saponification of soaps. These solutions would contain an excess of potassium hydroxide. For the copper or cobalt method of estimation described in this paper to be applied, this excess of potassium hydroxide would have to be neutralized with an acid such as hydrochloric. The solution would then contain an excess of potassium chloride. The effect of an excess of potassium chloride on the estimation was therefore investigated.

When sodium or potassium chloride was added to a methanol solution of the potassium salt of the higher fatty acids very little dissolved. This excess dissolved however when aqueous copper nitrate was added. The optical density of the chloroform extract of this solution, 0.41, was lower than for the control, 0.54, which contained no potassium chloride. The experiment was repeated but the excess of potassium chloride was filtered off before the addition of the reagent. In this case there was no lowering of the optical density, 0.63 and 0.64. These results show that while the small amount of sodium or potassium chloride which dissolves in methanol has no effect on the estimation, larger amounts interfere. Similar results were obtained using cobalt soaps. RALSTON[3] states that the presence of sodium chloride increases the solubility of calcium and magnesium soaps in water. This could explain the above results. If the solubility of the copper or cobalt soap in water is increased it will require more chloroform to extract all of the metallic soap. This is not the case. A second extraction with 10 ml chloroform removed no more colour. The potassium chloride must therefore interfere in another way.

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EXPERIMENTAL

Reagents

(1) 2% aqueous copper nitrate solution or 2% methanolic cobalt nitrate solution
(2) A.R. chloroform
(3) 0.1*N* methanolic potassium hydroxide
(4) Methanol

Apparatus

(1) Unicam SP600 spectrophotometer equipped with 1 cm glass cells
(2) Separating funnel
(3) Whatman No. 1 filter paper

Procedure using copper nitrate (range 0.008 to 0.04M)

The sample of fatty acid is weighed and dissolved in methanolic potassium hydroxide. The pH is adjusted by addition of more potassium hydroxide to about 9. Additional methanol is added to make the concentration of the solution in the range 0.008 to 0.04*M*. 5 ml of this solution are pipetted into a separating funnel. 10 ml of copper nitrate solution are added, when a blue precipitate is formed. 10 ml of chloroform and 5 ml of water are then added and the whole shaken vigorously. On settling, the blue lower layer of chloroform is run off. The presence of small amounts of water in the chloroform sometimes makes this solution somewhat cloudy. The solution is therefore filtered through Whatman No. 1 filter paper into the glass cells of the spectrophotometer which removes these traces of water. The optical density is then measured at 675 mμ against a chloroform blank.

Procedure using cobalt nitrate (range 0.04 to 0.2M)

The method is identical with the above copper method with the following exceptions.

1. The reagent is in methanolic and not aqueous solution as at the higher acid concentration addition of water causes precipitation of the fatty acid.

2. As the reagent is in methanol solution, 10 ml of water are added with the chloroform instead of 5 to ensure a separation into two layers.

3. The optical density is measured at 525 mμ.

Applications of the method

1. *Hydrolysis of esters*

Stearic acid formed by the hydrolysis of ethyl stearate was estimated by the copper method to check the application of this method to the estimation of fatty acids in the hydrolysate of esters. $\frac{1}{2}$ g of ethyl stearate was heated under reflux with 10 ml of *N* potassium hydroxide for 1 hour. The excess potassium hydroxide was neutralized with conc. hydrochloric acid and the pH adjusted to 9—10. A considerable precipitate of potassium chloride was formed. This was filtered off and the precipitate was thoroughly washed with methanol. The whole filtrate was made up to 100 ml. 5 ml of this solution was taken and treated as described in the experimental section. A calibration curve was obtained using pure stearic acid. The results are shown in Table II.

TABLE II

Method	*% purity of ethyl stearate*
Copper	99.8
Copper	99.5
Titration	97.5

2. *Saponification of resins*

Certain resins are known to contain abietic acid but no satisfactory way of estimating it is known. The hydrolysates of these resins are usually dark-brown in colour and potentiometric titrations often have indefinite end-points. The copper method was therefore applied to the hydrolysate of a resin. The hydrolysis method was as for ethyl stearate but the time of heating under reflux was increased to 4 hours. A calibration curve was obtained using pure abietic acid. The method showed that the resin contained 66% abietic acid. The saponification value for the same resin was 220 compared with 185 for pure abietic acid. This showed that the resin contained esters of lower molecular weight acids which were estimated by the saponification method.

3. *Analysis of emulsions*

Cosmetic and textile emulsions frequently contain such fatty acids as oleic and stearic together with organic bases such as triethanolamine and inorganic bases such as sodium or potassium hydroxide. The oleic acid content of one such emulsion was found. 10 ml of the emulsion was taken and alcoholic potassium hydroxide added until the pH was 9—10. The volume was then made up to 25 ml with methanol. 5 ml of this solution was treated with copper nitrate in the usual way. The result found by this method of 1.46% oleic acid agreed well with the theoretical value of 1.44%.

ACKNOWLEDGEMENT

The author is indebted to British Nylon Spinners Limited, for permission to publish these results.

SUMMARY

Two colorimetric methods of estimating the higher fatty acids C_7—C_{18} have been developed. One involves the formation of the copper soap and the other the cobalt soap. The amount of acid is found by measuring the optical density of chloroform solutions of the precipitated metallic soaps at 675 mμ for copper or 525 mμ for cobalt. In addition to the higher fatty acids, unsaturated fatty acids such as oleic acid and resin acids such as abietic acid may be estimated by these methods.

These methods have been applied to the (1) hydrolysates of esters and resins, (2) analysis of cosmetic and textile emulsions.

RÉSUMÉ

Deux méthodes sont proposées pour le dosage colorimétrique des acides gras supérieurs C_7—C_{18}. L'une est basée sur la formation d'un savon de cuivre et l'autre sur la formation d'un savon de cobalt. La teneur en acide est déterminée en mesurant la densité optique des solutions chloroformiques des savons métalliques précipités, à 675 mμ pour celui de cuivre ou à 525 mμ pour celui de cobalt. En plus des acides gras supérieurs, des acides gras non saturés tels que l'acide oléique et des acides résiniques, comme par exemple l'acide abiétique, peuvent être dosés par ces deux procédés.

Ces méthodes ont été appliquées (1) aux hydrolysats d'esters et de résines (2) à l'analyse des émulsions cosmétiques et textiles.

ZUSAMMENFASSUNG

Zwei kolorimetrische Methoden zur Bestimmung der höheren Fettsäuren C_7-C_{18} wurden entwickelt. Die eine gründet sich auf die Bildung einer Kupferseife, die andere auf diejenige einer Kobaltseife. Man bestimmt die Säuremenge durch Messung der optischen Dichte von Chloroformlösungen der gefällten Metallseifen, und zwar bei 675 mμ für Kupfer und bei 525 mμ für Kobalt. Ausser der höheren Fettsäuren können auch ungesättigte Säuren wie Oleinsäure und Harzsäuren wie Abietinsäure mit Hilfe dieser Methoden bestimmt werden.

Die Methoden wurden (1) für Hydrolysate von Estern und Harzen (2) zur Analyse von kosmetischen und Textilemulsionen angewendet.

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SUR LE MICRODOSAGE DES PEROXYDES DE CORPS GRAS PAR LA THIOFLUORESCÉINE

par

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Dans un travail précédent[1], nous avons montré que la thiofluorescéine (T.F.), étant décolorée quantitativement par l'iode, permettait le microdosage des peroxydes lipidiques avec une sensibilité très grande. Nous avons été progressivement amenés à modifier quelque peu la technique primitive qui donnait assez fréquemment des résultats aberrants. Nous décrirons d'abord une nouvelle technique qui a été utilisée depuis 5 ans pour plus de 10.000 dosages. Nous comparerons ensuite ces résultats avec ceux de la méthode classique, par libération d'iode et titrage au thiosulfate.

Réactifs

1. Chloroforme pur, contenant 0.5% d'alcool éthylique.

2. Solution de quelques mg de T.F. dans l'acétate d'éthyle redistillé. On la porte quelques minutes à l'ébullition, ce qui la rend stable plusieurs jours. Elle doit être ajustée de telle sorte que 0.1 ml dilué dans 10 ml de la solution ci-dessous donne une absorption convenable pour la mesure photométrique (concentration de l'ordre de $1^{0}/_{00}$).

3. Solution avec:

Carbonate de sodium cristallisé	94.5	g
Cyanure de potassium	0.33	g
Eau distillée	1 000	ml

On peut remplacer avantageusement le cyanure par la même quantité de „Complexon III".

4. Méthanol pur.

5. Solution à 10% d'acide benzoïque dans du chloroforme.

6. Solution saturée d'iodure de potassium, exempt d'iodates, lavée au chloroforme pour éliminer l'iode libre, et additionnée d'une goutte de NH_4OH au 1/10.

Technique du dosage

La réaction se fait dans un tube à centrifuger en verre mince, d'environ 2 cm de diamètre sur 10 cm de longueur. Le tube est fixé par un bouchon de liège sur un réfrigérant monté à reflux. Par le canal central de ce réfrigérant un tube mince de verre amène un courant de CO_2 chargé de vapeurs de chloroforme par passage préalable dans un barbotteur, qu'il est commode de lier de façon rigide au réfrigérant.

On dispose également d'un B.M. réglé à 70°-75°.

Dans le tube à réaction on introduit successivement:

2 ml de la solution chloroformique d'acide benzoïque,
1 ml de méthanol,
0.1 ml de la solution de T.F.

Le tube est mis en place sur l'appareil, de telle sorte que le CO_2 barbotte bulle à bulle dans le liquide. On attend une minute; on introduit 0.1 ml de la solution de KI; on fait barbotter encore quelques minutes; on fait descendre le tube à réaction de telle sorte que l'extrémité du tube

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adducteur soit à quelques millimètres au dessus de la surface du liquide. On dispose alors le B.M. à 70° de telle sorte que seul le fond du tube y soit plongé.

On laisse réagir 5 minutes. On enlève le B.M. que l'on remplace par un vase plein d'eau froide. On enlève alors le tube à réaction, on y ajoute 10 ml de la solution de carbonate. On agite vivement, on centrifuge à vitesse modérée. La phase aqueuse colorée est passée au spectrophotomètre à 5 900 Å dans une cuve de 1 cm d'épaisseur. On a ainsi la valeur du témoin.

On recommence la même opération après avoir ajouté dans le tube à réaction le corps gras à étudier. Une nouvelle mesure donne la valeur de l'essai.

Rappelons que les solutions alcalines de T.F. sont photosensibles. Il faut éviter de les exposer à la lumière solaire, et faire les mesures photométriques sans attendre.

Expression des résultats

Le coefficient d'absorption de la thiofluorescéine est extrêmement élevé: 10^{-8} at.-grammes d'iode amènent (lorsqu'ils sont, comme c'est le cas ici, ajoutés à la T.F. en milieu acide) une chute de la densité optique de 0.025, le volume liquide étant 10 ml et l'épaisseur 1 cm; 10^{-8} at.-grammes d'oxygène peroxydique donnent une chute double. On en déduit aisément que si m est la masse de corps gras mis en expérience, l'indice de peroxyde P est:

$$P = \frac{T-E}{5\,m}$$

expression dans laquelle T et E sont les valeurs de la densité optique ($\log \frac{I_0}{I}$) pour le témoin et l'essai.

En fait la valeur de 0.025 que nous indiquons comme correspondant à 10^{-8} at.-grammes d'iode n'est qu'une valeur moyenne, que l'on peut adopter pour des mesures courantes ou comparatives. La valeur réelle est généralement très voisine, mais certains échantillons de T.F. nous ont donné des valeurs allant de 0.020 à 0.030. Si on désire des valeurs absolues précises, il convient de mesurer cette „valeur en iode" à l'aide d'une solution titrée de ce métalloïde et de corriger en conséquence la relation que nous venons de donner.

Il est évident que la masse m est toujours très faible. On obtiendra par exemple avec un lipide d'indice 100 une chute d'absorption de 0.500 avec 1 mg de substance.

Comparaison de la méthode à la T.F. et de la méthode de KING, ROSCHEN ET IRWIN

Nous avons comparé les résultats donnés par cette méthode avec ceux de la technique de KING, ROSCHEN ET IRWIN[2]. Nous avons employé celle-ci soit selon la technique primitive, soit avec barbottage de CO_2. Deux substrats ont été essayés:

1. Acide linoléique, obtenu à partir d'huile de tournesol, par cristallisation fractionnée dans l'acétone[3]. L'étude par spectrophotométrie ultra-violette et l'indice d'iode y montrait l'existence de 0.73% d'acide linolénique, 90% d'acide linoléique, 4.4% d'acide oléique et 4.9% d'acides saturés.

2. Acide oléique, obtenu par le même procédé[4] à partir d'un produit commercial. L'analyse spectrale et l'indice d'iode conduisaient à la composition suivante: acide linoléique 0.42%; acide oléique 95%; acides saturés 4.6%.

L'oxydation a été faite à l'air, en couche mince, à 37° pour l'acide linoléique et les bas indices d'acide oléique; à 60° pour les indices élevés de ce dernier.

Les résultats sont donnés en indices de peroxyde dans le Tableau 1.

La plupart des dosages ont été faits en double. On voit que les trois méthodes donnent des valeurs qui ne diffèrent jamais de plus de ±3%, sans d'ailleurs que les écarts soient systématiques.

La précision de la méthode que nous venons de décrire dépend des faits suivants:

L'expérience montre qu'une opération complète (qu'il s'agisse du témoin ou de l'essai) donne des valeurs de densité optique reproductibles à 0.01 près.

TABLEAU I

	Méthode de KING *et coll.*				*Méthode à la T.F.*	
	Sans CO_2		*Avec CO_2*			
Acide oléique	1.5	1.5	1.5	1.5	1.42	1.37
	2.1	2.2	2.2	2.2	2.27	2.29
	2.8		2.8		2.53	2.69
	3.6		3.5		3.62	3.67
	51.9	51.0	51.0	51.0	54.1	52.8
	285	281	283	283	266	279
	304	301	300	301	285	298
Acide linoléique	11	11	11	12	11.9	12.1
	36	36	38	36	35.1	35.2
	152	152	152	152	147	145
	390	395	390	390	402	394

Le dosage résultant de la différence de deux mesures, l'erreur absolue est de 0.02; nous admettons 0.025. L'erreur relative sera évidemment d'autant plus faible que la chute d'absorption sera plus grande. Il est difficile en pratique de dépasser à cet égard 0.80. Les erreurs sur le dosage seront dans ce cas ± 1.5%.

RÉSUMÉ

Le microdosage des peroxydes par la thiofluorescéine, avec quelques modifications de la technique initiale, donne des résultats identiques, aux erreurs expérimentales près, à ceux de la méthode de KING, ROSCHEN ET IRWIN. Les essais ont été faits sur les peroxydes d'acide oléique et d'acide linoléique.

SUMMARY

The microdetermination of peroxides by thiofluorescein, with some modifications of the initial technique, gives results identical, within the limits of experimental error, with those obtained by the method of KING, ROSCHEN AND IRWIN. The tests were carried out on the peroxides of oleic and linoleic acids.

ZUSAMMENFASSUNG

Mikrobestimmungen von Peroxyden mit Thiofluorescein, mit einigen Abänderungen der anfänglichen Arbeitstechnik, ergaben, innerhalb der Fehlergrenze, dieselben Resultate wie die Methode von KING, ROSCHEN UND IRWIN. Die Versuche wurden mit Olein- und Linoleinsäure-Peroxyd ausgeführt.

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A D.C. ARC METHOD FOR THE SPECTROGRAPHIC DETERMINATION OF HAFNIUM IN ZIRCONIUM

by

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INTRODUCTION

Of the various methods available for spectrochemical analysis, the D.C. arc method of excitation has the advantage of simplicity, availability and rapidity. Though there are several methods[1,2,3,4,5,6] for the spectrochemical determination of Hf in Zr, only two[5,6] of these have used the D.C. arc. However, as the concentration ranges covered by them are 0.03 to 0.4%[5], and 2 to 50% HfO_2, it was decided to develop a D.C. arc method to cover the range 0.2 to 5%.

EXPERIMENTAL PROCEDURES

Preparation of standards

Standard samples were prepared following the method of SMITH AND SPITZER[7]. Known amounts of high purity zirconium and hafnium oxides were separately dissolved in hydrofluoric acid, taken to fumes with conc. H_2SO_4 and then diluted with water to a definite volume. Measured amounts of each solution were mixed and precipitated with NH_4OH. The co-precipitated hydroxides were filtered, dried and ignited for one hour at about 900° C. The resulting standard oxide mixtures were ground to minus 200 mesh (B.S.S.).

Eight standard samples with different hafnia content in the range 0.1 to 5% were prepared. The zirconium and hafnium oxides used were known to contain 80 ppm of hafnium and 130 ppm of zirconium respectively. For the purpose of these standards, these impurities were neglected and no correction was applied.

Standards were also prepared by dry mixing. Weighed amounts of each oxide were mixed in an agate mortar and sieved through 250 mesh (B.S.S.) sieve and the whole operation repeated three times. Standards so prepared were not unsatisfactory though a larger standard deviation of ± 8% was observed.

Operating conditions

The optimum experimental conditions found are summarized below:

Spectrograph	Hilger large Quartz — E 492
Wavelength range	2360 — 3240 Å
Focus	Source focussed behind slit by spherical lens
Slit width	0.01 mm
+ Lower electrode	Graphite rod 3/16″ diameter with central 1/8″ cavity, 4 mm deep
— Upper electrode	Tapered graphite rod 3/16″ dia.
Analytical gap	2 mm (adjusted optically)
Excitation source	D.C. arc at 15 amps 220 V; D.C. from rectified 440 V, 3 phase 50 cycle A.C.

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Amount of sample for each spectrum	5 mg
Pre-arcing period	nil
Time of exposure	15 seconds
Plates used	Kodak B10
Development	1.5 minutes at 78° F in D—19 by ordinary dish method
Line pair used	HfII 2861.696/ZrII 2856.065
Densitometer	Moll photographic recording microphotometer Type A.

Plate calibration

A seven step rotating sector with a step ratio of 2:1 placed immediately in front of the slit was used. From the values of the optical density of the different intensity steps, the calibration curve was drawn on the Respektra* and straightened using a transformation constant H = 0.65.

Working curve

The straightened plate calibration curve obtained was transformed into the working curve by suitably transferring the hafnia percentage scale on the Respektra. The working curve on the normal log-log scale is shown in Fig. 1.

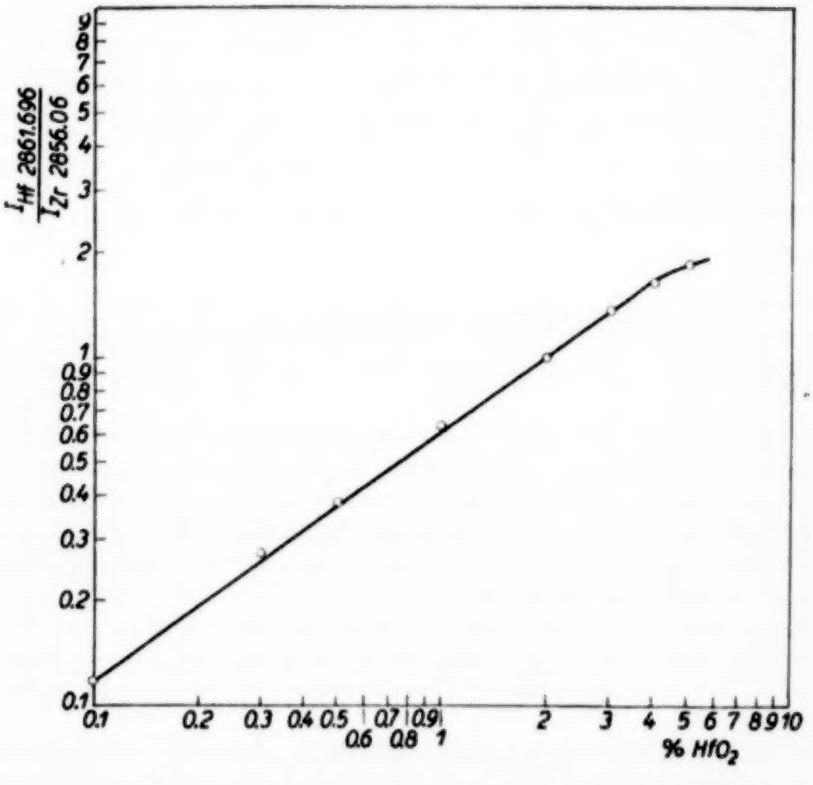

Fig. 1. Working curve for 0.2 to 5% HfO_2.

DISCUSSION

Selection of line pair

A literature search was made for suitable line pair or pairs that could be used to cover the range of 0.2% to 5% HfO_2. Various line pairs have been used by different investigators to cover this range, however only those line pairs were selected for study where the excitation source was a D.C. arc or discharges with arc-like characteristics. These are listed in Table I.

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* Trade name for spectrochemical calculator made by Dennert and Pape, Hamburg, Germany.

The line pair used by FASSEL AND ANDERSON[3] was found most suitable under the experimental conditions described above. There are three very weak Fe lines near the zirconium line but under normal conditions and up to about 0.5% Fe these do not interfere with the determination. The 2852.129 Å line of Mg and the 2852.828 and 2853.031 Å Na lines cause maximum interference, particularly when these elements are present in excess of about 1% and 2% respectively. The background of the zirconium line increases very rapidly with even small increases in the Mg content and analysis is not possible if it is 1% or more. In the case of sodium higher percentages can be tolerated. Al in excess of about 5% also interferes with the estimation by suppressing the excitation of Zr and Hf.

TABLE I

LIST OF LINE PAIRS TRIED WITH REMARKS REGARDING THEIR APPLICABILITY WHEN USING A D.C. ARC

Line pair	*Conc. range % Hf*	*Excitation conditions as used by*		*Remarks*
Hf 2820.3 (3rd order) Zr 2823.0 (3rd order)	0.1 to 0.4	D.C. arc at 30 A, 250 V	MORTIMORE AND NOBLE[6]	The 2823.0 Å line was not at all or barely excited at currents up to 20A, the maximum available to the present authors.
HfII 2638.710 ZrII 2640.151	2 to 50	D.C. arc	CHANDLER[5]	Not suitable for lower hafnia concentrations.
HfII 2641.406 ZrII 2647.8	0.01 to 1.0	Impulse arc	KINGSBURY AND TEMPLE[4]	Presence of weak lines made background correction difficult; results not very reproducible; standard deviation of 20%.
HfII 2548.2 Zr 2545.6	0.1 to 55	Impulse arc	KINGSBURY AND TEMPLE[4]	Severe interference from 2548.08 Å Fe line; also erratically excited in the D.C. arc.
HfII 2861.696 ZrII 2856.065	0.1 to 6.4	Arc-like interrupted discharge	FASSEL AND ANDERSON[3]	Very reproducible.

Background correction

As the samples were excited on graphite electrodes, there was sufficient background in most of the spectrograms comparable in density with the analysis lines particularly at lower concentrations. Hence background correction was made according to the "Seidel-function" transformation[8,9]. This was accomplished using the "U" scale of the Respektra, which is a scale of the Gaussian subtraction logarithms thus giving the Seidel transformations.

Accuracy

When the samples are free from impurities particularly Mg, Fe, Al and Na, a standard deviation of ±6% at about 1.5% HfO_2 is obtained, which increases to about 10% for samples containing small amounts of Mg, Fe, Al and Na.

Work on this problem is being continued to develop a method for the analysis of hafnia content down to about 0.003%.

SUMMARY

A spectrographic method is presented for the quantitative determination of hafnium in zirconium in the range 0.2% to 5% HfO_2. The sample in the form of a fine powder is burnt in a D.C. arc at 15 amp., 220 V, and the spectrum photographed with a large quartz spectrograph. The hafnia concentration is determined from the ratio of the intensities of the spectral lines HfII 2861.696 Å and ZrII 2856.065 Å. A standard deviation of ± 6% has been obtained by this method for samples essentially free from other impurities, especially Fe, Al, Mg and Na.

RÉSUMÉ

Une méthode spectrographique est proposée pour le dosage quantitatif du celtium dans le zirconium, pour des teneurs allant de 0.2 à 5% de CtO_2. L'échantillon, sous forme de poudre fine, est brûlé dans un arc de 15 amp., 220 V; le spectre est photographié au moyen d'un spectrographe à prisme de quartz. La concentration en oxyde de celtium est obtenue en déterminant le rapport des intensités des lignes spectrales CtII 2861.696 Å et ZrII 2856.065 Å. Une déviation standard de ± 6% a été obtenue par cette méthode pour des échantillons exempts d'autres impuretés, spécialement Fe, Al, Mg et Na.

ZUSAMMENFASSUNG

Eine spektrographische Methode zur quantitativen Bestimmung von Hafnium in Zirkonium, für Gehalte von 0.2—5% HfO_2 wurde vorgeschlagen. Die Probe wird in Form eines feinen Pulvers in einem Bogen von 15 A, 220 V verbrannt und das Spektrum wird mit einem grossen Quarz-Spektrographen photographiert. Die HfO_2-Konzentration bestimmt man aus dem Verhältnis der Intensitäten der Spektrallinien HfII 2861.696 Å und ZrII 2856.065 Å. Mit dieser Methode wurde für Proben, welche frei von anderen Verunreinigungen, insbesondere Fe, Al, Mg und Na sind, eine Standardabweichung von ± 6% erhalten.

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POLAROGRAPHY OF TETRAVALENT GERMANIUM*

by

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Reduction of tetravalent germanium at the d.m.e. has already been reported, among others, by VALENTA AND ZUMAN[1], and DAS GUPTA AND NAIR[2]. The former workers recommended EDTA complexing media for a suitable analytical procedure. This paper presents the results obtained in a somewhat detailed study of the process in non-complexing media.

From Latimer's standard potential data the reduction of germanic acid in alkaline medium appears to proceed as follows[3]:

$$HGeO_3^- + 2H_2O + 4e \rightarrow Ge^\circ + 5(OH)^- \qquad (1)$$

Single step reduction waves could be observed in our study up to a pH as low as 5 in sodium acetate-acetic acid buffer. At lower pH, only hydrogen discharge interferes. Two interesting characteristics of the process that have been observed are: (a) an anomalous contribution to the current analogous to that already reported by ORLEMANN AND KOLTHOFF and (b) a retarding effect on the cathode process in the absence of a sufficient concentration of supporting electrolyte.

EXPERIMENTAL

GeO_2 of 99.95% purity (New Metal Co., England) was dissolved in distilled water and made into a stock solution of 25 millimolar strength. Other reagents were of A.R. or C.P. grades and found to be polarographically inert in the range of our studies.

Polarograms were obtained with an automatic pen-recording Tinsley apparatus using a conventional H-type cell. Before each run purified nitrogen was passed through the solution thermostated at 30° ± 0.1° C. Wave-heights were measured by the tangential method given by STACKELBERG[4]. Plots of log $i/(id\text{-}i)$ *Vs* E were made to determine halfwave potentials and slopes of such plots. Since the cell was found to have an ohmic resistance insignificant for our purpose, no IR correction was made.

A Beckman model H-2 pH meter was used for the pH measurements.

Results

Of the four buffers tried, phosphate, carbonate, acetate and borate, the last was preferred for the wide working range (pH 6 and upwards) it provides. Below pH 6, acetate buffer was used. Experiments with phosphate buffer showed that the discharge of supporting electrolyte takes place rather early. Also, at a higher concentration of phosphate ($> 0.3M$ for $2\cdot10^{-4}M$ Ge), the waveheight is depressed indicating the possible formation of a complex between the depolarizer and the phosphate ion. In a recent paper by EVEREST AND SALMON[5], published after completion of this work, the authors have also postulated the formation of the orthophosphate complex of germanium.

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* Presented as abstract to the 42nd Session of the Indian Science Congress, January 1955.

In Fig. 1, curves 1-7 show the nature of reduction waves of germanium under various conditions. Curves 3, 4 and 5 show that the addition of KCl increases the waveheight. This is, however,

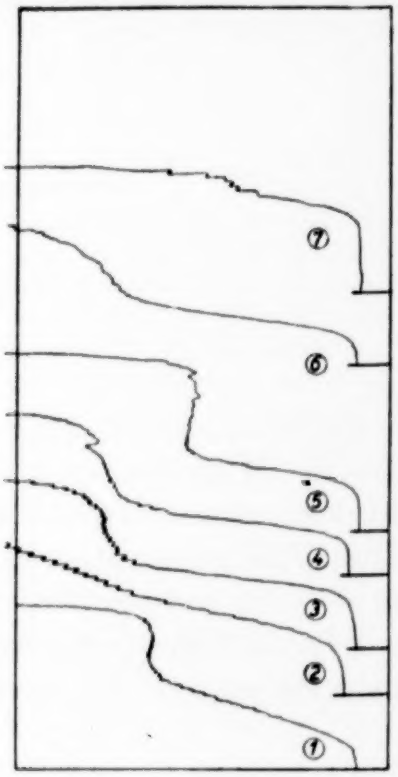

Fig. 1. Curves 5 and 7 start from —1.10 V and —1.00 V respectively. The rest from —1.20 V.

Curve 1: Ge = $1 \cdot 10^{-2}M$, KCl = $0.5M$, pH 6.2, gelatine = 0.005%, Sn 20.*
Curve 2: Ge = $2 \cdot 10^{-4}M$, boric acid $0.25M$, pH 6.2, Sn 5.
Curve 3: Ge = $2 \cdot 10^{-4}M$, boric acid $0.1M$, KCl $0.1M$, pH 6.2, Sn 5.
Curve 4: Ge = $2 \cdot 10^{-4}M$, boric acid $0.25M$, pH 8.15, Sn 5.
Curve 5: Ge = $2 \cdot 10^{-4}M$, boric acid $0.1M$, KCl $2M$, pH 8.2, Sn 10.
Curve 6: Ge = $2 \cdot 10^{-4}M$, boric acid $0.25M$, KCl $1M$, pH 8.0, gelatine 0.005%, Sn 5.
Curve 7: Ge = $2 \cdot 10^{-4}M$, Na acetate $0.1M$ + acetic acid, pH 4.85, Sn 10.

TABLE I

EFFECTS OF UNI-UNIVALENT AND DI-UNIVALENT SALTS ON WAVEHEIGHT AND HALF-WAVE POTENTIAL

KCl	(0.1) 15.75	(0.3) 18.5	(0.5) 19.5	(1) 22.25 —1.400	(2) 24.5 —1.396	(3) 28 —1.373	(3.5) 28.5 —1.368
$NaClO_4$	(1) 22.25 —1.383	(2) 24.25 —1.350	(3) 24 —1.325	(4) 21.5 —1.296	(5) 20 —1.288		
$CaCl_2$	(0.7) 21.5 —1.326	(0.9) 21.5 —1.296	(1) 22 —1.292	(2) 18.25 —1.242	(3) 11.5 —1.225		
$BaCl_2$	(0.65) 22.25 —1.310	(0.90) 23 —1.303					
$SrCl_2$	(0.62) 20.5 —1.315	(0.86) 20 —1.289					
$MgCl_2$	(0.66) 21 —1.355	(0.92) 20.5 —1.346					

Ge = $2 \cdot 10^{-4}M$, boric acid = $0.1M$, pH adjusted to 8.2 for solution containing 0.1, 0.3 and $0.5M$ KCl, and 6.6—6.8 for the rest. The figures in parentheses denote the concentration in molarities of the salts added, corresponding waveheight in arbitrary unit and half-wave potential (S.C.E.) stand vertically below in the respective order.

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* Sn denotes sensitivity.

not observed in the presence of gelatine (curve 6). Gelatine in its usual dosage also shifts the polarograms to more negative values, the magnitude of the shift increasing with addition of more gelatine. The effects of different uni-univalent and di-univalent electrolytes as supporting media on the $E\frac{1}{2}$ and wave height are tabulated in Table I.

Dependence of the wave height on the height of mercury column

In the following media, each containing $2 \cdot 10^{-4}M$ Ge: (a) $0.25M$ boric acid, adjusted to pH 8.0 with KOH, (b) $0.25M$ boric acid + $2M$ KCl adjusted to pH 8.0 as above, and (c) same as (b) + 0.005% gelatine, $I/\sqrt{h}$ remained constant within 2% for (a) and (c) between column heights 38 and 68 cm; while for (b) the value progressively increased by 40%. Thus, in the absence of an appreciable concentration of a foreign electrolyte, or in the presence of gelatine, a pure diffusion controlled wave is observed.

Effect of pH on $E\frac{1}{2}$ and I_d

Fig. 2, curves *a* & *b*, show the above effects.

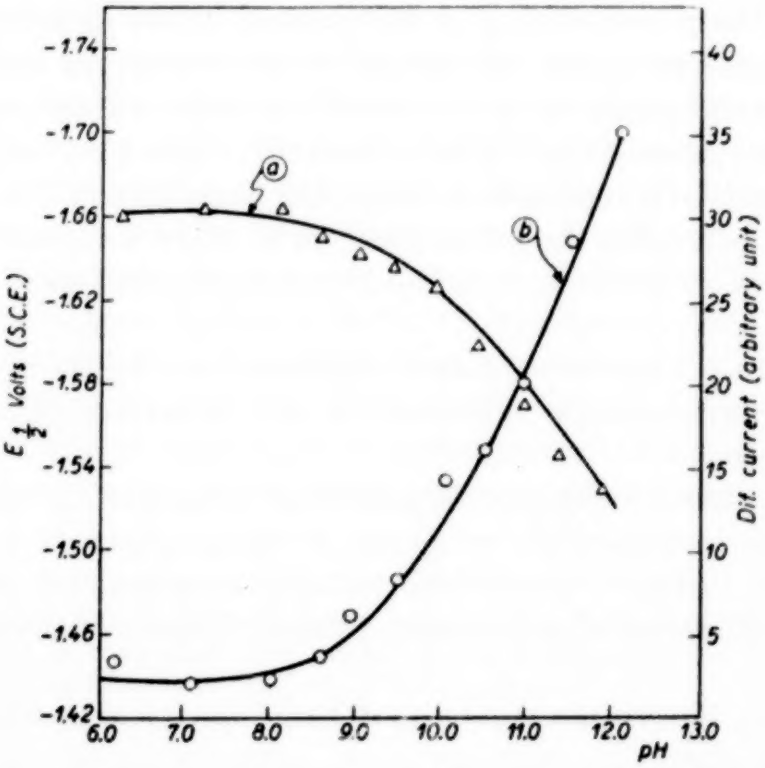

Fig. 2. Effects of pH on diffusion current and half-wave potential.

Curve a: Ge = $2 \cdot 10^{-4}M$, boric acid = $0.1M$, KCl = $0.1M$, gelatine = 0.005%. pH adjusted by addition of KOH.

Curve b: Ge = $2 \cdot 10^{-4}M$, boric acid = $0.25M$, KCl = $0.1M$, pH adjusted as above.

Diffusion current constant

In a typical solution containing $2 \cdot 10^{-4}M$ Ge, $0.25M$ boric acid, $0.1M$ KCl and 0.005% gelatine, adjusted to pH 8.2 with KOH, the D.C.C. value was found to be 7.35.

Table II shows the constancy of I/c under various conditions. In the presence of gelatine the

TABLE II

CONSTANCY OF I/c

Concentration range (M)	*Supporting medium*	*$I(\mu A)/c(mM)$ average*
a) $3 \cdot 10^{-5}$ — $8 \cdot 10^{-4}$	Boric acid $0.25M$ + KOH, pH 8.15	15
b) $2 \cdot 10^{-4}$ — $5 \cdot 10^{-3}$	Boric acid $0.25M$, KCl $1M$, gelatine 0.005%, + KOH, pH 8.0	15
c) $3 \cdot 10^{-5}$ — $2 \cdot 10^{-4}$	Boric acid $0.25M$, KCl $2M$, + KOH, pH 7.8	26

waves become markedly flattened, specially at lower concentrations of germanium. In the series (c), above $2 \cdot 10^{-4} M$ Ge, I/c steadily decreases with increasing concentration of Ge. The scaler of the recording chart sets a limit to our experiments at a maximum Ge concentration of $5 \cdot 10^{-3} M$ (series b). For analytical application, this range and condition (addition of gelatine) should be of value.

The $E\frac{1}{2}$ values for different concentrations of germanium under the same condition are approximately the same. The slope in a typical polarogram, corresponding to curve 3, Fig. 1, is —0.060, indicating the high irreversibility of the wave.

DISCUSSION

Assuming equation (1) as representing the reduction mechanism, the $E\frac{1}{2}$ should be pH-dependent, which is actually the case. The non-uniformity may, however, be attributed to the irreversibility of the process. Since i_d decreases at higher pH, reduction in unbuffered media will result in an ununiform increase of pH at the cathode vicinity and consequently the resultant wave will be smaller in magnitude and with a greater negative slope (Fig. 1, curve 1). Curves 2-4 may be interpreted by assuming an electrostatic repulsion between the cathode and the negatively charged depolarizer ions. Increasing the pH or addition of $0.1 M$ KCl, each supplying a sufficient concentration of electrolyte to nullify the potential gradient forces, gives a normal wave.

Effect of gelatine on the waves may be explained on the basis of HEYROVSKY AND MATYAS'[6] interpretation on the inhibitory action of surface films on the reduction of polyvalent cations.

The D.C.C. observed is nearly double that obtained for Ge^{+2} by EVEREST[7]. This supports the four-electron reduction. A likely alternative mechanism in the reduction of Ge^{+4} to Ge^{+2}, which may be disproportionated to Ge^{+4} in alkaline medium and is again reduced, is discounted due to absence of any kinetic contribution to the wave.

Further equating KOLTHOFF AND ORLEMANN'S[8] empirical equation on water waves, it may be shown that:

$$\frac{i_{t_1}}{i_{t_2}} = \sqrt{\frac{h_1}{h_2}} \; \frac{1 - K m_2^{-1/3} T_2^{-4/3}}{1 - K m_1^{-1/3} T_1^{-4/3}} \qquad (2)$$

where i_{t_1} and i_{t_2} represent the total currents at mercury heights h_1 and h_2 ($h_2 > h_1$); m_1, m_2 and T_1, T_2 represent the corresponding masses of mercury and drop times respectively.

$$\text{Since} \quad \frac{1 - K m_2^{-1/3} T_2^{-4/3}}{1 - K m_1^{-1/3} T_1^{-4/3}} < 1, \; \frac{i_{t_1}}{i_{t_2}} < \sqrt{\frac{h_1}{h_2}} \quad \text{or} \quad \frac{i_{t_1}}{\sqrt{h_1}} < \frac{i_{t_2}}{\sqrt{h_2}} \qquad (3)$$

Relation (3) is in agreement with our observation. On the basis of a microcoulometric study, MEITES[9] has recently interpreted such anomalous currents as being of the nature of condenser current.

That the condenser current is observed in a total supporting electrolyte concentration as low as $0.2 M$ may be due to the higher charge of the central ion of the depolarizer as well as the liberation of OH^-. As is also seen from the data the condenser current is proportional to the diffusion current only up to a limited extent.

The decrease of i_d at higher pH values may be interpreted by assuming the existence of several species of germanic acids at different pH ranges. From the data of EVEREST AND SALMON[10], and from other literature reports the following pH dependent equilibrium is suggested:

$$\begin{matrix} HGeO_3^- & \rightleftarrows & HGe_5O_{11}^- & \rightleftarrows & HGeO_3^- & \rightleftarrows & Ge(OH)_6^{-2} \\ \text{pH } 6 & \longleftrightarrow & \text{pH } 9.4 & \longleftrightarrow & \text{pH } 11 & \longleftrightarrow & \text{higher pH} \end{matrix}$$

The ion $Ge(OH)_6^{-2}$ which is increasingly formed at higher pH may be considered irreducible. The slight decrease in waveheight between pH 8.5 and 9.5 may, however, be due to the lower diffusion coefficient of the pentamer, which is the principal species.

The trend of the shift of $E\frac{1}{2}$ to less negative potentials by addition of foreign electrolytes qualitatively supports the views of DELAHAY AND MATTAX[11].

It is observed that the total current is generally higher in the presence of monovalent electrolytes. In the light of MEITES' view on the origin of the condenser current as being due to the extra energy expended in reforming and maintaining the electrical double layer around a drop against disruption by the water molecules, it seems logical to assume that the double layer formed with cations of higher charge density should be relatively more rigid, and the condenser current consequently lower in magnitude. Sodium, having a higher charge density than potassium, causes lesser non-faradic current as is also seen from the data. In these experiments no correction has been made for viscosity of the media. Clearly, for a solution of calcium chloride, this factor will be appreciable[12]. Appropriate corrections in this direction may significantly improve the nature of the empirical relation derived in such studies.

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SUMMARY

The polarographic reduction of germanic acid has been studied in aqueous boric acid solutions and in several other buffer media. The reduction takes place by four electrons. The effects of pH in the range 6-12 on the diffusion current and half-wave potential support the postulation of the existence of several species of germanic acids involved in a pH dependent polymerization-depolymerization equilibrium in the system. The data, obtained under specified conditions, can be utilized for the polarographic estimation of Ge^{+4}.

RÉSUMÉ

La réduction polarographique de l'acide germanique a été examinée dans des solutions aqueuses d'acide borique et dans plusieurs autres solutions tampon. Quatre électrons interviennent dans la réduction. L'effet du pH (de 6 à 12) sur le courant de diffusion et le potentiel $E\frac{1}{2}$ confirme l'existence de plusieurs espèces d'acides germaniques (équilibre de polymérisation-dépolymérisation dépendant du pH). Les valeurs obtenues dans des conditions déterminées peuvent être utilisées pour le dosage polarographique de Ge^{+4}.

ZUSAMMENFASSUNG

Die polarographische Reduktion der Germaniumsäure wurde in wässrigen Borsäurelösungen und in verschiedenen anderen Pufferlösungen untersucht. Die Reduktion geschieht durch 4 Elektronen. Die Einflüsse des pH's zwischen 6 und 12 auf den Diffusionsstrom und das Potential $E\frac{1}{2}$ stützen die Annahme, dass es mehrere Arten von Germaniumsäuren gibt, die mit einander in einem pH-abhängigen Polymerisation-Depolymerisations-Gleichgewichte stehen. Die unter genau umschriebenen Bedingungen erhaltenen Ergebnisse können zur polarographischen Bestimmung von Ge^{+4} dienen.

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ANALYTICAL APPLICATIONS OF THE CHEMICAL ACTION OF LIGHT

III. NEW VOLUMETRIC DETERMINATION OF URANIUM(VI) THROUGH PHOTOCHEMICAL REDUCTION BY LACTIC ACID

by

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In recent years GOPALA RAO and coworkers have initiated the planned use of the chemical action of light in quantitative chemical analysis. GOPALA RAO AND RAMACHARLU[1] proposed the determination of mercuric chloride through its photochemical reduction by sodium oxalate in sunlight or artificial light, the resulting mercurous chloride being estimated iodometrically. GOPALA RAO AND MADHUSUDHANA RAO[2] have carried out the determination of ferric salts by reducing them with oxalic acid in sunlight and titrating the resulting ferrous salt with a standard solution of sodium vanadate. GOPALA RAO, ARAVAMUDAN AND VENKATAMMA[3] showed that lactic acid can be used for achieving the quantitative photochemical reduction of ferric salts in sunlight or artificial light. GOPALA RAO AND ARAVAMUDAN[4] have shown that in nearly neutral solutions mandelic and citric acids rapidly reduce ferric salts quantitatively to the ferrous state in sunlight or artificial light and that the ferrous salt can be accurately determined by titration with a standard solution of sodium vanadate. We have now studied the photochemical reduction of uranium(VI) salt in sunlight and in artificial light with oxalic, tartaric, formic, citric and lactic acids with a view to its analytical application.

The photochemical decomposition of various organic acids under exposure to ultraviolet light from a quartz mercury vapour lamp or sunlight has been the subject of study by numerous workers. Such investigations have been carried out both in the presence and absence of uranyl salts, which act as photosensitizers. Studies with oxalic, malonic, formic and lactic acids have been concerned mostly with the determination of the quantum efficiency, temperature coefficient and the mechanism of the reaction. The emphasis in these studies was on the mode of photochemical decomposition of the organic acid and not so much on the reduction of the uranium(VI) salt, which was used in most of the experiments at relatively very low concentrations for its photosensitizing action. BOLIN[5] noticed that uranium(VI) salts are reduced to the uranium(IV) stage in the presence of lactic acid and light. HATT[6] established the formation of uranium(IV) salt during the photochemical decomposition of uranyl formate. WEISS[7] has also observed the reduction of uranium(VI) salt to uranium(IV) stage during the photosensitized decomposition of oxalic acid in visible light.

Now, it appeared to us that the photochemical reaction between the uranium(VI) salt and an organic acid can be employed for the quantitative estimation of uranium (VI) salt. This will be possible if the uranium(VI) salt is rapidly and quantitatively reduced to the uranium(IV) stage and if a suitable volumetric procedure can be devised for the oxidimetric estimation of uranium(IV) salt thus obtained in the presence of the organic acid and its photochemical decomposition products. With this end in view, we have investigated the use of formic, oxalic, tartaric, citric and lactic acids, as photochemical reductants. The reaction with lactic acid has been found to be particularly useful from the analytical stand point. Consequently this reaction has been pursued in detail. We have been able to standardize the conditions, under which it is possible to achieve the quantitative reduction of the uranium(VI) salt with lactic acid in the presence of sunlight or the light from a Philip's Repro Lamp.

EXPERIMENTAL

Materials employed

The uranyl acetate used in this investigation is of the A. R. grade, manufactured by Mallinckrodt Chemical Works, New York, and is stated to conform to A.C.S. specifications. The uranyl acetate solutions were standardized gravimetrically through the oxinate or volumetrically by the KOLTHOFF AND LINGANE method. All the other chemicals used are also of the analytical reagent grade.

Analytical method for the determination of uranium(IV) salt

A mixture of uranyl acetate solution, sodium salt of the organic acid and dilute sulphuric acid was exposed to light in a 100 ml pyrex glass beaker, for the prescribed period and the uranium (IV) salt formed was titrated with a standard sodium vanadate solution using diphenylbenzidine as indicator, after adding excess of ferric alum solution and sufficient phosphoric acid. Alternatively, the uranium(IV) was titrated directly with standard sodium vanadate solution with N-phenyl anthranilic acid or diphenylbenzidine as inside indicators under conditions described hereafter. Potassium permanganate, ceric sulphate or potassium dichromate may not be used for this determination, because the unreacted organic acid and its photochemical decomposition products may react with the oxidant either directly or through an induced mechanism. Even sodium vanadate has not been found to be suitable for the estimation of the uranium(IV) salt formed by the photochemical reduction of uranium(VI) salt with tartaric acid. The photochemical decomposition products of tartaric acid cause serious interference during the titration of uranium(IV) salt even with sodium vanadate. For this reason the photoreduction of uranium (VI) salt with tartaric acid is not useful from the analytical stand point, although the reaction is very rapid.

Photochemical reduction in sunlight

5.0 ml of about $0.0125M$ uranium acetate solution was mixed with 5.0 ml of $0.2M$ solution of the sodium salt of the organic acid, 5.0 ml of 10 N sulphuric acid and 5.0 ml of water. The mixture was exposed to bright sunlight in a pyrex glass beaker covered with a watch glass. After the solution was exposed to sunlight for the required time, it was withdrawn and titrated with a standard solution of sodium vanadate. The results are given in Table I.

TABLE I

Amount of uranium(VI) salt taken = 0.0650 millimole exposed for 120 minutes to sunlight.

Amount of addendum	*Amount of uranium(IV) salt formed in millimoles*	*Percentage reduction*
1.0 millimol oxalic acid	0.0045	6.9
1.0 millimol citric acid	0.0135	20.9
1.0 millimol lactic acid	0.0585	90.0

Experiments in the light from a Repro lamp

Messrs. Philips of Holland have introduced a high pressure Mercury Vapour Lamp which gives a good intensity of actinic light. This lamp is conveniently set up and worked on the A.C. mains of a laboratory unlike the old mercury vapour lamps. In our experiments, we have used a high pressure Mercury Vapour Lamp with a glass bulb, marketted under the name "Repro Lamp". The results of comparative experiments on the photoreduction of uranyl salts with different organic acids under the Reprolamp are given in Table II.

TABLE II

2.0 ml of $0.0225\,M$ uranyl acetate solution + 5.0 ml of $0.1\,M$ solution of sodium salt of the organic acid + 2.5 ml of $5\,N$ sulphuric acid — diluted to 25 ml and exposed to the light from a Repro Lamp for 10 minutes and then titrated with a standard solution of sodium vanadate. Amount of uranium(VI) salt taken = 0.045 millimoles

Amount of addendum	*Amount of uranium(IV) salt formed in millimoles*	*Percentage reduction*
0.5 millimole of oxalic acid	Nil	Nil
0.5 millimole of formic acid	0.0020	4·4
0.5 millimole of citric acid	0.0025	5.6
0.5 millimole of lactic acid	0.0200	44·4

From the results in Tables I and II it is seen that the speed of the photochemical reduction with oxalic acid is negligible; with formic and citric acids it is measurable but not rapid enough for analytical purposes.

Influence of varying acid concentration. Experiments have been conducted to study the influence of varying the sulphuric acid concentration on the speed of photochemical reduction of uranium (VI) salt with lactic acid. The results are given in Table III.

TABLE III

2.0 ml of $0.0225\,M$ uranyl acetate solution + 5.0 ml of $0.1\,M$ sodium lactate solution + requisite volume of $5\,N$ sulphuric acid + water to make up to 25 ml — exposed to the Repro Lamp for 10 minutes.

Overall concentration of sulphuric acid (N)	*Amount of uranium(IV) salt formed in millimoles*
0.10	0.0201
0.25	0.0202
0.50	0.0202
1.00	0.0201
2.00	0.0203
Theoretical	0.0450

From the results in Table III, it appears that variation of the concentration of sulphuric acid has not much effect on the speed of the photochemical reduction, in the concentration limits $0.1\,N$ to $2.0\,N$. Experiments are in progress on the photochemical reduction of uranyl lactate in neutral medium or very nearly neutral medium.

Influence of lactate concentration. We have carried out experiments under the Repro Lamp to study the effect of varying the concentration of sodium lactate on the speed of the photochemical reduction. The results are given in Table IV.

TABLE IV

2.0 ml of $0.0225\,M$ uranyl acetate solution + requisite amount of sodium lactate solution + 2.5 ml of $5\,N$ sulphuric acid + water to make up to 25 ml — exposed for 30 minutes under the Repro Lamp. Amount of uranium(VI) taken = 0.045 millimoles.

Mole ratio of U(VI): lactate	*Amount of uranium(IV) formed in millimoles*
1 : 0.50	0.0095
1 : 0.67	0.0113
1 : 1.00	0.0189
1 : 1.50	0.0225
1 : 2.00	0.0320
1 : 3.00	0.0351
1 : 4.00	0.0355

From Table IV, it is evident that the speed of the photochemical reaction between uranium(VI) and lactic acid reaches almost a constant value when the concentration of lactic acid is taken at about 3 or 4 times that of uranium(VI).

Experiments in monochromatic light

The results recorded in Table V show that wave lengths longer than 4300 Å are not effective for the photochemical reduction of uranium(VI) salts by lactic acid. Different spectral regions have been isolated with the help of filters supplied by Photovolt Corporation, New York, in conjunction with a Philips' Repro Lamp.

TABLE V

2.0 ml of $0.0225M$ uranyl acetate + 5.0 ml of $0.1M$ sodium lactate + 5.0 ml of $5N$ sulphuric acid + water to make upto 25 ml — exposed for 45 minutes.

Average wave length	*Amount of uranium(IV) salt formed in millimoles*
6500 Å	Nil
5300 Å	Nil
4900 Å	Nil
4300 Å	0.0200
3800 Å	0.0206
Theoretical	0.0450

Interference of foreign ions

We have found that fluoride does not exert any inhibiting influence on the course of the reaction, except that it precipitates the uranous salt in the absence of sufficient acid concentration. However, if sufficient sulphuric acid is added, the precipitate dissolves; fluoride does not also interfere in the subsequent titration with sodium vanadate. Chlorides and bromides inhibit the photochemical reduction of uranium(VI) even when present at small concentration. Consequently the photochemical reduction of uranium(VI) cannot be achieved with lactic acid in hydrochloric acid medium. Perchloric acid is found to have no effect on the photoreduction. Phosphoric acid, too, does not interfere with the photoreduction. In this case, it is necessary to add sufficient sulphuric acid or phosphoric acid to prevent the formation of a green jelly in the course of the photochemical reduction. Arsenate does not interfere either with the reduction or with the titration of uranium(IV) formed with sodium vanadate.

Photochemical volumetric determination of uranium(VI)

A large number of determinations of uranium(VI) salt have been carried out by the new method now developed. Typical results are presented in Table VI. The procedure adopted consists in exposing an aliquot of uranium(VI) salt solution with excess lactic acid, 5.0 ml of $5.0N$ sulphuric acid and enough water to make up to 25 ml, for one hour in a pyrex glass beaker under a Philips Repro Lamp. It is desirable to have enough lactic acid to give a mole ratio of uranium (VI): lactic acid = 1 : 4 or more. After exposure the solution is titrated with $0.025N$ sodium vanadate solution, using N-phenyl anthranilic acid (two drops of 0.1% solution) as inside indicator, keeping the overall sulphuric acid concentration at $6.0N$. Diphenylbenzidine or diphenylamine sulphate (0.5 ml of 0.1% solution) can also be used as inside indicators in this titration, if 5 ml of syrupy phosphoric acid and 2.0 ml of $1.0N$ oxalic acid are added to the titration mixture. In the absence of phosphoric acid and oxalic acid, diphenylbenzidine or diphenylamine sulphonate does not give a sharp indication of the end-point in the direct titration of uranium(IV) salt by sodium vanadate.

TABLE VI

Amount of uranium salt taken in millimoles	*Amount of uranium salt found in millimoles*
0.0125	0.0124
0.0250	0.0248
0.0375	0.0373
0.0500	0.0448
0.0750	0.0746
0.1000	0.0996
0.2038	0.2036

The results in Table VI show that the new method now proposed enables one to determine uranium(VI) with an accuracy comparable to other well known methods of procedure.

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SUMMARY

A new volumetric method for the determination of uranium(VI) has been developed. The method consists in exposing the uranium(VI) salt in 1.0-2.0*N* sulphuric acid solution with an excess of lactic acid to sunlight or to the light of a Philips Repro Lamp for one hour. The uranium (IV) salt formed by reduction is estimated by titration with a standard solution of sodium vanadate with N-phenyl anthranilic acid as redox indicator. One important advantage of the new method is that the U(VI) salt is not reduced to the U(III) stage under any conditions. Fluoride, phosphate and arsenate do not interfere. Chloride, bromide, tungstate and molybdate interfere.

RÉSUMÉ

Une nouvelle méthode de dosage volumétrique de l'uranium (VI) est proposée. Elle consiste à exposer un sel de l'uranium(VI), en solution dans l'acide sulfurique 1.0 à 2.0*N*, en présence d'un excès d'acide lactique, à la lumière solaire ou à celle d'une lampe Philips Repro pendant une heure. L'uranium(IV), formé par réduction, est dosé par une solution étalon de vanadate de sodium, en présence d'acide N-phénylanthranilique comme indicateur rédox. Un avantage important de cette nouvelle méthode est que l'uranium(VI) n'est pas réduit en uranium(III). Les anions fluorhydrique, phosphorique et arsénique ne gênent pas. Les chlorures, bromures, tungstates et molybdates gênent.

ZUSAMMENFASSUNG

Eine neue volumetrische Bestimmungsmethode für Uran(VI) wird vorgeschlagen. Sie besteht darin, dass das Uran(VI)-Salz in 1.0 bis 2.0*N* Schwefelsäurelösung und in Gegenwart eines Überschusses an Milchsäure während einer Stunde dem Sonnenlichte oder dem Lichte einer Philips Repro Lampe ausgesetzt wird. Das durch Reduktion gebildete Uran(IV)-Salz wird dann mit einer eingestellten Natriumvanadatlösung und in Gegenwart von N-Phenylanthranilsäure als Redoxindikator titriert. Ein grosser Vorteil dieser neuen Methode ist, dass das Uran(VI) nicht zu Uran(III) reduziert wird. Fluorid-, Phosphat- und Arseniationen stören nicht, während Chlorid-, Bromid-, Wolframat- und Molybdationen stören.

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DIALLYLDITHIOCARBAMIDO-HYDRAZINE AS AN ANALYTICAL REAGENT

PART II. DETERMINATION OF COPPER, ZINC AND NICKEL IN THE PRESENCE OF IRON AND URANIUM

by

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In Part I of this series[1], the determination of copper, nickel, zinc and lead and their separation in binary mixtures under specified pH conditions have been described. Separation of copper, zinc and nickel from iron and uranium and the study of the effects of chloride and nitrate ions on their quantitative precipitations form the subject matter of the present communication. Chloride and nitrate ions do not interfere, nor do iron and uranium when present in small quantities.

EXPERIMENTAL

E. Merk 'Pro Analysis' chemicals were used.

Separation of copper from iron and uranium

Stock solutions of iron and uranium were prepared by dissolving solid ferric alum in dilute sulphuric acid and uranium acetate in distilled water.

A measured volume of copper solution was mixed with a measured volume of ferric (or uranium) solution. The solution was neutralized with excess dilute ammonia solution, and ferric hydroxide was precipitated. The main bulk of the precipitate was redissolved in dilute sulphuric acid, giving the solution a slight smell of ammonia. The solution was then treated with dilute citric acid until the remaining ferric hydroxide just dissolved, and warmed slightly on a water bath until clear. It was then diluted to 200 ml and cooled. Copper was precipitated by the reagent solution, during continuous stirring. It was then allowed to settle for about 2 hours, filtered, washed and dried at 105° C as usual.

TABLE I

	Fe added g	*U added* g	*Wt of Cu compound* g	*Cu taken* g	*Cu found* g
1	0.02		0.1158	0.02528	0.02522
2	0.025		0.1162	0.02528	0.02530
3	0.05		0.1238	0.02701	0.02696
4	0.02		0.1864	0.04045	0.04059
5		0.1	0.1244	0.02701	0.02709
6		0.1	0.1488	0.03239	0.03241
7		0.1	0.1740	0.03779	0.03789

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Separation of zinc from iron and uranium

Measured volume of zinc solution and ferric (or uranium) solution were taken in a 400 ml beaker. The solution was then neutralized as before and the precipitated ferric hydroxide dissolved in dilute citric acid. The solution was diluted to 200 ml and, after adding reagent solution in slight excess, heated on a water-bath. At first no precipitate appeared, then 3 g of sodium acetate were added, followed by dropwise addition of a solution of caustic soda (about 0.4 g for each precipitation). Zinc was completely precipitated, allowed to settle for 2 h, filtered, washed and dried as usual.

TABLE II

	Fe added g	*U added* g	*Zn compound* g	*Zn taken* g	*Zn found* g
1	0.02		0.1883	0.04175	0.04191
2	0.02		0.0942	0.02088	0.02097
3	0.02		0.1135	0.02505	0.02527
4		0.1	0.0943	0.02088	0.02099
5		0.1	0.1128	0.02505	0.02511
6		0.1	0.1686	0.03758	0.03753

Estimation of nickel in the presence of iron

Procedure was the same as that for the zinc and iron mixture. In this case 1 g of sodium acetate was added and this was followed by the dropwise addition of a solution of 0.2 g of solid caustic soda in water. The nickel compound was then filtered, washed and dried as usual.

TABLE III

	Fe added g	*Wt of Ni compound* g	*Ni taken* g	*Ni found* g
1	0.002	0.1911	0.03777	0.03787
2	0.003	0.1015	0.03777	0.03797
3	0.003	0.3068	0.06042	0.06075
4	0.003	0.3442	0.06797	0.06828

The results given in the above tables indicate that copper, zinc and nickel can be determined even in the presence of iron, when present in small quantities. This observation is important, since commercial binary alloys like brass (Cu-Zn) and monel metal (Cu-Ni) always contain iron, though not as a constituent but as an impurity and to the extent of about 2-3%. Hence, the above results indicate that our method is also well suited for gravimetric analysis of such commercial alloys because the tolerable limits of iron in the analyses are quite above those present in such alloys.

Effect of Cl^- ion and NO_3^- ion on the determination of Cu and Ni

It has been found that these ions do not interfere with the determinations. This was studied by the addition of weighed quantities of KCl or KNO_3 to the starting solutions.

TABLE IV

	Amount of salt g	*Cu taken* g	*Cu found* g	*Ni taken* g	*Ni found* g
1	1 KCl	0.02606	0.02596		
2	25 ,,	0.02606	0.02611		
3	2 KNO_3	0.02606	0.02594		
4	2 ,,	0.02606	0.02607		
5	2 KCl			0.03772	0.03747
6	2 ,,			0.03772	0.03757
7	2 KNO_3			0.03772	0.03741
8	2 ,,			0.03772	0.03777

SUMMARY

It has been observed that copper, zinc and nickel can be quantitatively precipitated by diallyldithiocarbamido-hydrazine even in the presence of iron and uranium when these are present in small quantities. Chloride and nitrate ions do not interfere. Results indicate that our method is also well suited for gravimetric analysis of alloys like brass and monel metal.

RÉSUMÉ

Le cuivre, le zinc et le nickel peuvent être quantitativement précipités par la diallyldithiocarbamido-hydrazine, même en présence de fer et d'uranium en faibles quantités. Les ions chlorhydrique et nitrique ne gènent pas. Les résultats obtenus montrent que notre méthode est avantageuse pour l'analyse gravimétrique d'alliages tels que le laiton et le métal Monel.

ZUSAMMENFASSUNG

Kupfer, Zink und Nickel können durch Diallyldithiocarbamido-hydrazin quantitativ gefällt werden, und zwar auch in Gegenwart kleiner Mengen von Eisen und Uran. Chlorid- und Nitrat-Ionen stören nicht. Die Ergebnisse zeigen, dass diese Methode auch zur gravimetrischen Analyse von Legierungen wie Messing und Monelmetall geeignet ist.

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DETERMINATION OF TITANIUM BY CUPFERRON WITH COMPLEXONE III AS THE MASKING AGENT

by

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The reagent cupferron introduced by O. BAUDISCH[1] was used for quantitative analysis because it provided complete precipitation and separation of iron, vanadium, zirconium, titanium, tin, columbium, tantalum, tetravalent uranium and presumably hafnium, from others such as aluminium, beryllium, phosphorus, boron, manganese, nickel and sexivalent uranium, in strong acid solution. Copper and thorium were also determined by the reagent in very weak acid solution but the methods were not very satisfactory compared to other techniques. Lead, silver, mercury, bismuth, cerium, thorium, tungsten, and in certain cases when present in excessive amounts, silica, phosphorus, alkaline earths and alkali salts, interfere[2].

LUNDELL AND HOFFMAN[3] studied the precipitation of various elements by the reagent in solutions which were made 3.5-4.5N in sulfuric or hydrochloric acid; the elements that were completely precipitated were titanium, vanadium, zirconium, columbium, tantalum, molybdenum, hafnium, tungsten, iron, palladium, gallium, tin, antimony, bismuth and polonium. Elements which were partially precipitated included copper, thallium, thorium, protoactinium, actinium, lanthanum and other metals of the rare earth group. In addition, uranium, phosphorus, and silicon may interfere under certain conditions.

The influence of the idea of the existence of the so-called "Lewis Acids" led SCHWARZENBACH[4] to study the complex cations, the stability constants of which were found to increase with the replacement of simple individual ligands by a bidentate group, and the increase was much greater if a 5-membered chelate ring could be formed than if a 6-membered or a still larger one were formed. Tridentate, quadridentate, pentadentate and hexadendate groups added to metal cations frequently cause the adducts to have extremely large stability constants.

A study was made[4] of several aminopolycarboxylic acids with a polydentate group, capable of forming 5-membered rings with metal cations. Ethylenediaminetetraacetic acid (di-sodium salt) being a hexadentate with two basic nitrogen and four carboxyl groups formed highly stable and usually soluble complexes with the metallic ions. The stability of the complexes in general diminished rapidly with the decrease in atomic number of the metal along a horizontal period of the Periodic Table; the aminopolycarboxylic acids, on the other hand, were characterized by their ability to form complexes not only with the alkaline earths but even with lithium and sodium.

Přibil and Schneider[5] utilized the chelating agent ethylenediaminetetraacetic acid (di-sodium salt) to keep the elements, iron, aluminium, mercury, copper, lead, bismuth, cadmium and nickel in solution during the precipitation of titanium as hydroxide. Pickering[6] modified the method somewhat for quicker precipitation of titanium, suggesting the use of magnesium salt as a demasking agent (*cf.* [7]).

This paper deals with the estimation of titanium by cupferron in the presence of quite a large number of elements masked by the disodium salt of ethylenediaminetetraacetic acid, commonly known as complexone III, from a faintly ammoniacal medium or preferably in the presence of ammonium acetate-acetic acid buffer. It has thus been possible to separate titanium from arsenite, borate, molybdate, vanadate, tungstate, arsenate, large excess of alkali salts, alkaline earths, magnesium, lead, copper, bismuth, cadmium, zinc, manganese, nickel, cobalt, antimony, iron, aluminium, chromium, zirconium, thorium, and rare earths including cerium. Hexa- and tetravalent uranium, tin (stannous and stannic) and beryllium are precipitated along with the titanium, which can also be separated from tungstate and trivalent antimony in the presence of tartrate even without complexone III. Phosphate interferes, but the alkaline earth metals do not interefere under the condition of precipitation with ammonium acetate.

EXPERIMENTAL

Reagents and standard solutions

Chemicals used were all of highest purity.

Reagents

(a) 6% solution of cupferron in cold water, (b) 10% solution of complexone III (di-sodium salt of ethylenediaminetetraacetic acid) in water, (c) dilute solution of ammonia prepared by the passage of ammonia gas into cold water, (d) 20% solution of ammonium acetate in water.

Standard solutions

(i) A solution of titanium sulphate was prepared from potassium titanium oxalate by decomposing it with sulphuric acid in the presence of ammonium sulphate[8]. The titanium sulphate solution so prepared was made up to a definite volume and the titanium content of an aliquot portion of the solution was determined as oxide (TiO_2) by the cupferron method[9] of precipitation.

(ii) Solutions of other ions such as Na^+, K^+, Ca^{+2}, Sr^{+2}, Ba^{+2}, Cd^{+2}, Pb^{+2}, Fe^{+3}, Al^{+3}, Cr^{+3}, Zr^{+4}, Th^{+4}, Mg^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, VO_4^{-3}, AsO_3^{-3}, AsO_4^{-3}, $B_4O_7^{-2}$, MoO_4^{-2}, WO_4^{-2} were prepared from the respective salts and those of Sb^{+3}, Zn^{+2}, Cu^{+2} and Bi^{+3} from metals. The strengths of the solutions were determined by the well known standard procedures.

Rare earths including cerium (ous) were obtained from monazite sand and were freed from thorium, purified as oxalate and dissolved in hydrochloric acid in the presence of hydrogen peroxide and then standardized as mixed oxide (R_2O_3).

Procedure

An acid solution of titanium, alone or containing other ions from which it was to be separated, was mixed with an excess (10-15 times) of complexone III sufficient to keep the titanium and the interfering ions in solution. It was then made faintly ammoniacal to litmus or, better still, treated with sufficient excess of ammonium acetate after the addition of complexone III till the solution gave a distinctly yellow colour when tested with methylorange. This solution was diluted to 300-400 ml, cooled to 10° C and to it was added slowly with vigorous stirring the cupferron solution till the titanium precipitation was complete. The solution was then filtered, washed with cold water containing a little quantity of cupferron, dried, ignited carefully to oxide and weighed.

An excess of ammonia should be avoided during precipitation, as titanium was incompletely precipitated from strongly ammoniacal solution.

For separation from tungstate and antimony, the acid solution was treated first with tartaric acid and then, with or without the addition of complexone III, was rendered alkaline to methyl orange with ammonium acetate before it was ready for precipitation.

Under the conditions described above a few experiments were carried out to determine the higher pH regions for complete precipitation of titanium and it was found that in the presence of complexone III quite accurate results could be obtained if the pH range was between 4.3 and 7.0.

Results

TABLE I

pH RANGE FOR COMPLETE PRECIPITATION OF TITANIUM

No.	*TiO_2 taken* *mg*	*pH*	*TiO_2 found* *mg*
1	5.4	4.28	5.4
2	10.8	4.50	10.8
3	16.2	7.08	16.2
4	6.6	7.3	6.5

TABLE II

SEPARATION OF TITANIUM FROM OTHER IONS

Nos.	*TiO_2 taken* *mg*	*Ions added* *mg*	*TiO_2 found* *mg*	*Ions found* *mg*
1	86.8	Fe_2O_3 — 495.6	86.6	Fe_2O_3 — 496.0
2	52.0	578.2	51.8	577.6
3	86.8	Cu — 500.0	86.6	Cu — 498.0
4	21.7	300.0	21.6	298.3
5	82.0	V_2O_5 — 368.0	82.0	V_2O_5 — 367.0
6	14.8	184.0	15.0	183.8
7	26.0	ZrO_2 — 464.0	25.9	ZrO_2 — 462.0
8	14.8	185.6	15.0	185.0
9	35.5	Bi — 196.6	35.8	Bi — 196.6
10	22.2	245.8	22.2	246.2
11	23.3	Al_2O_3 — 333.0	23.3	Al_2O_3 — 332.4
12	38.8	MoO_3 — 391.6	38.8	MoO_3 — 392.0
13	29.1	352.4	29.0	352.0
14	26.0	ThO_2 — 304.0	26.0	ThO_2 — 302.8
15	20.8	244.0	20.9	242.0
16	13.0	PbO — 247.6	13.0	PbO — 247.6
17	39.0	742.8	39.1	741.8
18	13.0	Cr_2O_3 — 253.2	13.0	—
19	39.0	506.3	39.2	—
20	5.4	As_2O_3 — 100.0	5.4	—
21	10.8	200.0	10.7	—
22	5.4	As_2O_5 — 920.7	5.4	—
23	13.0	Sb — 197.2	13.1	Sb — 196.6
24	26.0	394.4	25.9	395.7
25	10.8	WO_3 — 110.3	10.8	WO_3 — 109.8
26	16.2	220.6	16.1	220.4
27	10.8	R_2O_3 — 200.0	10.9	—
28	16.2	250.0	16.2	—
29	10.8	Zn — 200.0 CdO — 120.5 MnO — 84.5 MgO — 200.0 NiO — 317.5 CoO — 254.0	10.8	—
30	10.8	B_4O_7 — 498.3	10.8	
31	16.2	830.5	16.0	

Separations from iron, copper, zirconium, bismuth, aluminium, thorium, vanadate and molybdate were performed both from solutions rendered just alkaline to litmus with ammonia and from solutions made alkaline to methyl orange with excess of ammonium acetate, which was used solely for the control of pH in the case of other separations (*cf.* Procedure).

Iron, vanadium and zirconium in the filtrate could be determined, after acidifying with conc. HCl, by the usual cupferron method, while for the others the organic matter in the filtrate was first completely destroyed by digestion with nitric and sulphuric acids and then the elements were determined by the standard procedures.

SUMMARY

The reagent cupferron has been found to be effective for the separation of titanium from Zr^{+4}, Th^{+4}, Fe^{+3}, Al^{+3}, Cr^{+3}, rare earths, Pb^{+2}, Cu^{+2}, Cd^{+2}, Bi^{+3}, Sb^{+3}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Mg^{+2}, Ca^{+2}, Ba^{+2}, Sr^{+2}, alkalis, AsO_3^{-3}, AsO_4^{-3}, VO_4^{-3}, MoO_4^{-2}, WO_4^{-2} and $B_4O_7^{-2}$ in the presence of complexone III at a pH between 4.3 and 7.0. Tin (II and IV), uranium (IV and VI), beryllium and phosphate interfere.

RÉSUMÉ

Le cupferron, en présence de complexon III, s'est montré très efficace pour la séparation du titane d'avec les ions suivants: Zr^{+4}, Th^{+4}, Fe^{+3}, Al^{+3}, Cr^{+3}, terres rares, Pb^{+2}, Cu^{+2}, Cd^{+2}, Bi^{+3}, Sb^{+3}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Mg^{+2}, Ca^{+2}, Ba^{+2}, Sr^{+2}, métaux alcalins, AsO_3^{-3}, AsO_4^{-3}, VO_4^{-3}, MoO_4^{-2}, WO_4^{-2} et $B_4O_7^{-2}$. La séparation doit s'effectuer entre les pH 4.3 et 7.0. L'étain (II) et (IV), l'uranium (IV) et (VI), le béryllium et l'anion phosphorique gênent.

ZUSAMMENFASSUNG

Das Reagenz Cupferron ist in Gegenwart von Komplexon III zur Trennung des Titans von folgenden Ionen sehr wirksam: Zr^{+4}, Th^{+4}, Fe^{+3}, Al^{+3}, Cr^{+3}, seltene Erden, Pb^{+2}, Cu^{+2}, Cd^{+2}, Bi^{+3}, Sb^{+3}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Mg^{+2}, Ca^{+2}, Ba^{+2}, Sr^{+2}, Alkalimetalle, AsO_3^{-3}, AsO_4^{-3}, VO_4^{-3}, MoO_4^{-2}, WO_4^{-2} und $B_4O_7^{-2}$. Die Trennungen sollen bei pH 4.3-7.0 ausgeführt werden. Zinn (II und IV), Uran (IV und VI), Beryllium und Phosphationen stören.

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THE THERMOLYSIS OF THE 8-QUINOLINOL CHELATES OF YTTRIUM AND THE RARE EARTH ELEMENTS

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INTRODUCTION

The use of 8-quinolinol as a precipitant for metal ions in solution is well known in analytical chemistry. Although not a specific precipitant, under controlled conditions of hydrogen ion concentration, separations of certain metal ions can be achieved. 8-Quinolinol will in general precipitate the same metals as does ammonium hydroxide, hence it is to be expected that the rare earth metals will also be precipitated.

The first application of 8-quinolinol to the analytical determination of the rare earth metals was made by PIRTEA[1] who found that lanthanum was quantitatively precipitated from an ammoniacal solution. The precipitated chelate was either dried at 130° and determined gravimetrically or bromometrically titrated. The composition of the chelate was given as $La(C_9H_6NO)_3$, containing 24.33% La.

Cerium has also been determined as the 8-quinolinol chelate. PIRTEA[2] found that when a cerium(III) solution was precipitated with 8-quinolinol, the cerium was oxidized to the cerium(IV) oxidation state. The precipitated chelate had the formula, $Ce(C_9H_6NO)_4.2H_2O$, containing 18.73% Ce. The results which were obtained in 14 experiments in which the precipitate was weighed were excellent. It was also stated that since it took such a long time to convert the cerium(III) to cerium(IV), it was more practical to ignite the initial precipitate to CeO_2. With this latter method good results were obtained in 10 analyses.

To prevent the difficulties due to oxidation of the cerium(III) during precipitation, BERG AND BECKER[3] added an excess of hydroxylamine hydrochloride before the addition of the 8-quinolinol. Completing the precipitation from a tartrate buffered solution, the formula of the chelate was found to be $Ce(C_9H_6NO)_3$. The precipitate was dried at 110° and determined gravimetrically.

Since the precipitation of metal ions by 8-quinolinol is dependent on the pH of the solution, early investigators sought a method for the separation of the individual rare earth ions using this reagent. The first attempt along these lines was by MANNELLI[4] who found that cerium(III) could be separated from thorium by proper control of the hydrogen ion concentration of the solution. MISUMI[5] found that the minimum pH for the quantitative precipitation of lanthanum by 8-quinolinol from an ammonium succinate-ammonium hydroxide buffer was 7.1. With cerium(III) from an ammonium tartrate-ammonium hydroxide buffer the minimum pH was 9.4. It was stated that cerium(IV) did not form a chelate under these conditions. In a later paper, MISUMI[6] reported that lanthanum was precipitated by 8-quinolinol in the pH range 9.4 to 11.5 using a sodium citrate-ammonium hydroxide buffer.

The pH ranges for the precipitation of lanthanum and cerium were again subjected to investigation by ESWARANARAYANA AND RAGHAVA RAO[7]. They found pH ranges quite different from the previous studies. Lanthanum began to precipitate at pH 4.8 and was completely precipitated at pH 5.75. Cerium(III) was found to begin to precipitate at pH 5.55. Thorium could be separated from lanthanum and cerium by precipitation with 8-quinolinol at pH 3.9.

The determination of yttrium as the 8-quinolinol chelate was recently reported by MURTHY, SARMA AND RAGHAVA RAO[8]. For the gravimetric determination, yttrium was precipitated in the pH range of 5-6. The resulting precipitate, $Y(C_9H_6NO)_3$, was either weighed after drying at 100° for 4 to 6 hours or after ignition to Y_2O_3 at an unspecified temperature.

DUVAL[9] has studied the 8-quinolinol chelates of lanthanum and cerium on the thermobalance. In the case of the lanthanum chelate, the thermolysis curve descended all the way to 276°, at which temperature there was charring and considerable release of gas. In another sample, the thermobalance was held at 130°, the temperature indicated by PIRTEA[1], and a good horizontal obtained. With the cerium chelate, $Ce(H_9C_6NO)_4.2H_2O$, after removal of the adhering water, a horizontal was obtained from 128 to 233°. Above this temperature, the chelate decomposed with charring and evolution of gas. It was stated that the drying temperature of 110° given by BERG AND BECKER[3] was slightly too low to be certain of constant weight.

Because of the limited knowledge available on the thermolysis of the chelates and the disagreement on the data already known, the 8-quinolinol chelates of yttrium, lanthanum, cerium(III), praseodymium, neodymium, samarium and gadolinium were subjected to thermolysis on the thermobalance. Since the methods of preparation and the composition of the chelates varied over wide limits depending on the precipitation conditions, the method of homogeneous precipitation[10] was introduced as a standardized procedure for the precipitation of the 8-quinolinol chelates of these metal ions.

EXPERIMENTAL

Chemicals. 8-Quinolinol (m. p. 74-76°) was obtained from the Matheson, Coleman and Bell Co., East Rutherford, N. J. It was used without further purification.

The rare earths were obtained as the oxides of greater than 99% purity from the Lindsay Chemical Co., West Chicago, Ill., and Research Chemicals, Inc., Burbank, Calif.

Yttrium chloride of 99% purity was obtained from Research Chemicals, Inc., Burbank, Calif. All other reagents were of analytical reagent grade quality.

Thermobalance. The construction and operation of the thermobalance has been previously described[11,12].

Preparation and thermolysis of the chelates

Two procedures were used to prepare the 8-quinolinol chelates. The first was the procedure of PIRTEA[1] which was used to prepare the lanthanum 8-quinolinol chelate. The precipitated chelate was dried at room temperature (25 to 27°) for 24 h before thermolysis on the thermobalance.

The second procedure was by homogeneous precipitation. To a solution containing 0.1 to 0.3 g of the metal chloride in 200 ml of water were added 2 ml of 6N HNO_3 and 20 ml of a 4% solution of 8-quinolinol in 2N acetic acid. To this solution was added 6 g of urea, stirred well, and placed on a steam bath for about 5 h. At the end of this time the metal 8-quinolinol chelate had collected on the bottom of the beaker as a crystalline yellow precipitate. After cooling, the precipitate was collected on a sintered porcelain crucible, washed three times with water and air dried at room temperature for about 24 h.

The chelates were analysed for metal content by ignition to the corresponding metal oxide. The procedure consisted of weighing out 0.2 to 0.3 g samples of the chelate into tared platinum crucibles, adding 0.5 g of oxalic acid and igniting to constant weight at 800° in a muffle furnace. The chelates corresponded to the general formula, $M(C_9H_6NO)_3$; where M was Y, La, Ce(III), Pr, Nd, Sm and Gd.

DISCUSSION

The thermolysis curves are shown in Figures 1 and 2. In general, the curves are similar in appearance. The only exception is curve 1 of Figure 1 which shows the thermolysis of lanthanum 8-quinolinol prepared by the method of PIRTEA[1]. This curve is in qualitative agreement with the results of DUVAL[9] only that the temperatures recorded in this study are higher. The curve shows that excess 8-quinolinol is given off beginning at about 50° and is completely removed at about 220°. From this point to about 390° the chelate is stable. Oxidation of organic material begins at about 400° and is complete at about 700° where the oxide, La_2O_3, appears as a horizontal. Obviously, a large amount of 8-quinolinol was coprecipitated with the chelate. The first portion of this curve is very similar to the thermolysis of the pure reagent as found in an earlier study[13]. Since it is quite difficult to prevent coprecipitation of the reagent in the precipitate, this method cannot be recommended for the determination of lanthanum.

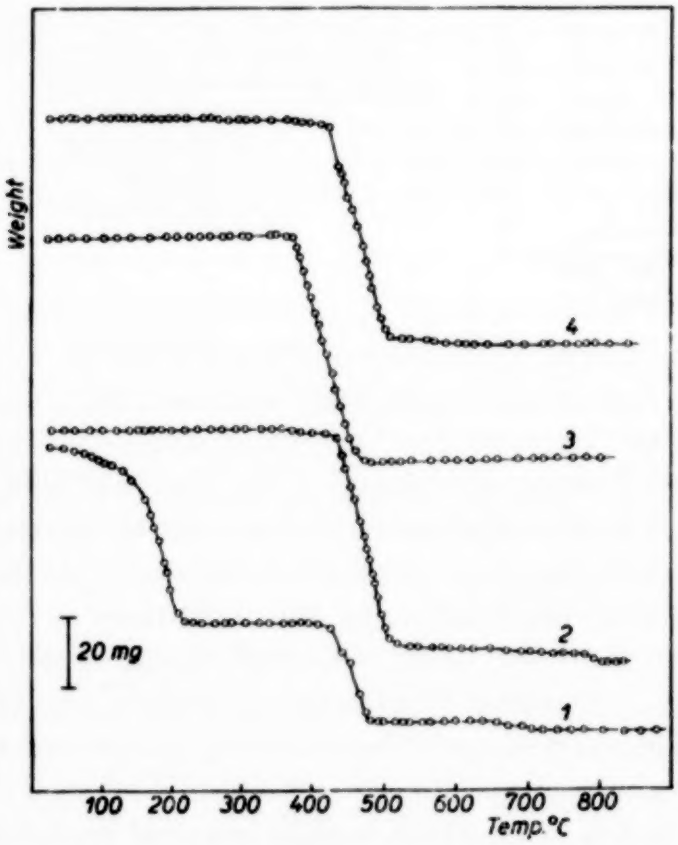

Fig. 1. The thermolysis curves of the 8-quinolinol chelates of the rare earth metals.
(1) lanthanum
(2) lanthanum
(3) cerium(III)
(4) praseodymium

The remaining seven thermolysis curves are of chelates which were precipitated by the method of homogeneous precipitation and are all similar in appearance. The decomposition of these chelates can be classified into three stages: (I) a small loss in weight (about 1%) in the temperature range 250 to 300°; (II) the oxidation of the organic material in the temperature range 350 to 525°; (III) the formation of the oxide in the temperature range 700 to 800°. These three stages can be found in all of the chelates except cerium(III).

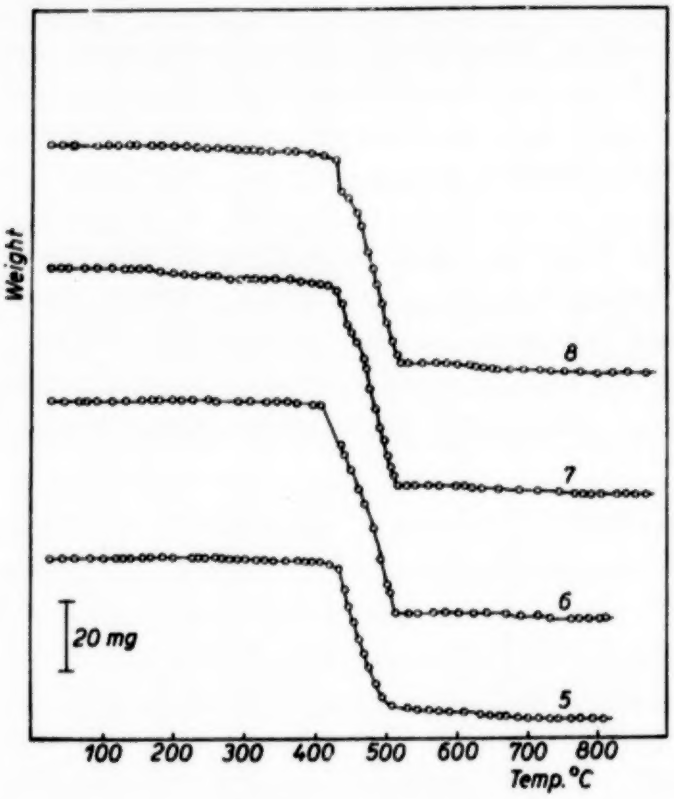

Fig. 2. The thermolysis curves of the 8-quinolinol chelates of yttrium and the rare earth metals.
(5) samarium
(6) neodymium
(7) yttrium
(8) gadolinium

The temperature limits of the three stages of decomposition are given in Table I. The chelates are anhydrous up to the first stage where there is a one percent loss in weight due to the decomposition of the chelate. In the second stage, the organic material begins to oxidize in all of the chelates. The slopes of the curves at this point are all about the same in magnitude. The decomposition product left in the thermobalance pan is not the pure oxide but contains some unoxidized carbonaceous matter. This is slowly oxidized as the temperature increases until the third stage is reached where the oxide level begins. Since the limit of the thermobalance is 900°, the curves were stopped at from 850 to 900°. It would be interesting to see if any further decomposition would occur if the temperatures could be extended to 1000 or 1100°.

The analytical significance of the thermolysis curves can readily be seen. Since the work of DUVAL[9] showed that a region of constant weight was not found in the lanthanum chelate, it was therefore not recommended for the determination of this

TABLE I

DECOMPOSITION TEMPERATURES FOR THE RARE EARTH 8-QUINOLINOL CHELATES

$M(C_9H_6NO)_3$	*Stage I* °C	*Stage II* °C	*Stage III* °C
Lanthanum	360	420-510	800
Cerium(III)	350	—	420
Praseodymium	280	320-520	575
Neodymium	250	330-510	730
Samarium	260	410-500	700
Gadolinium	250	400-525	755
Yttrium	175	370-525	740

References p. 113

metal ion. However, the results of this study show that there is indeed a region of constant weight which extends up to the first stage of the thermolysis curve. The 8-quinolinol chelates can be weighed as the compound represented by the general formula, $M(C_9H_6NO)_3$, if heated to constant weight in the temperature limits specified. If desired, the chelates can also be ignited to their respective oxides by ignition at higher temperatures.

It is interesting to note that the thermolysis curves of gadolinium and yttrium are very similar to each other, yet differ slightly from the other chelates. An identical situation was found in the thermolysis of the neocupferron chelates of the rare earth elements[12]. In this case also, the gadolinium and yttrium curves were very similar to each other but different from the others in this group.

SUMMARY

The thermolysis of the 8-quinolinol chelates of yttrium, lanthanum, cerium(III), praseodymium, neodymium, samarium, and gadolinium were studied on the thermobalance. It was found that the thermolysis of the chelates proceeded in three stages: (1) a small loss in weight (about 1%) in the temperature range 250 to 300°; (2) the oxidation of the organic material in the temperature range 350 to 525°; (3) the formation of the oxide in the temperature range 700 to 800°.

The method of homogeneous precipitation was introduced to form chelates corresponding to the general formula, $M(C_9H_6NO)_3$. The rare earth metals can be weighed in this form or ignited to the oxides in the temperature ranges specified by the thermolysis curves.

RÉSUMÉ

La thermolyse des chélates de l'hydroxy-8-quinoléine avec les éléments suivants: yttrium, lanthane, cérium(III), praséodyme, néodyme, samarium et gadolinium, a été étudiée sur la thermobalance. On remarque que la thermolyse des chélates se fait en 3 stades: (1) une faible perte de poids (environ 1%) entre les températures 250 et 300°; (2) l'oxydation de la partie organique entre 350 et 525°; (3) la formation de l'oxyde entre 700 et 800°.

La méthode par précipitation homogène a été introduite pour la formation des chélates, correspondant à la formule générale $M(C_9H_6NO)_3$. Les métaux des terres rares peuvent être pesés sous cette forme, ou calcinés à l'état d'oxydes aux températures indiquées par les courbes de thermolyse.

ZUSAMMENFASSUNG

Die Thermolyse der 8-Hydroxychinolin-Chelate von Yttrium, Lanthan, Cer(III), Praseodym, Neodym, Samarium und Gadolinium wurde mit Hilfe der Thermowaage untersucht. Es wurde festgestellt dass die Thermolyse dieser Chelate in drei Stadien verläuft: (1) ein geringer Gewichtsverlust (ungefähr 1%) bei 250-300°, (2) die Oxydation des organischen Materials bei 350-525°, (3) die Bildung des Oxydes bei 700-800°.

Die Methode der homogenen Fällung wurde zur Bildung von Chelaten mit der allgemeinen Formel $M(C_9H_6NO)_3$ eingeführt. Die Metalle der seltenen Erden können entweder in dieser Form gewogen werden oder bei den durch die Thermolyse-Kurven angegebenen Temperaturen zum Oxyd kalziniert werden.

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ANALYTICAL USE OF THE ^{27}Al (α, n) ^{30}P REACTION

by

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The nuclear reaction ^{27}Al (α, n) ^{30}P, discovered in 1934 by CURIE AND JOLIOT[1], has been used by us as a possible tool of analysing the Al content in various materials. Specimens containing Al were irradiated with ^{210}Po which emits alpha particles of about 5.3 MeV energy and has a half-life of 138.4 days[2]. As discussed in an earlier paper[3] this low energy of the incident alpha particles permits nuclear reactions leading to radioactive nuclides of appreciable yield only in boron, fluorine, sodium, magnesium and aluminium. Of the induced activities that from sodium is short-lived (^{26}Al, 6.3 sec) and that from fluorine is long-lived (^{22}Na, 2.6 years) compared with the 2.5 minutes activity induced in aluminium. The presence of Na and F, therefore, does not seriously disturb the measurements. The activity induced in boron has 10.3 minutes half-life (^{13}N) and that induced in magnesium has 2.4 min half-life (^{28}Al). It is therefore essential that these elements are absent in the specimen examined. As regards Mg, it is the isotope ^{25}Mg, which gives ^{28}Al. As ^{25}Mg forms 10.1 per cent of natural magnesium a small contamination of Mg may be tolerated. (For details about nuclear properties we have consulted the review of HOLLANDER, PERLMAN AND SEABORG[4].)

The reaction ^{27}Al (α, n) ^{30}P is known to be endothermic with a Q value of —2.9 MeV[5]. After the incident alpha particles have lost kinetic energy to about 3.4 MeV; they are therefore not active in producing ^{30}P.

EXPERIMENTAL PROCEDURES

Our irradiations were performed in a manner indicated in Fig. 1. The polonium alpha source (originally about 160 mC, finally about 15 mC) described in detail earlier[3] was placed at a carefully measured distance from the specimen.

The irradiations were performed during 300 ± 2 seconds. The specimens were then introduced in a Geiger-Müller counter and the counting started 20 ± 2 seconds after finishing the irradiation.

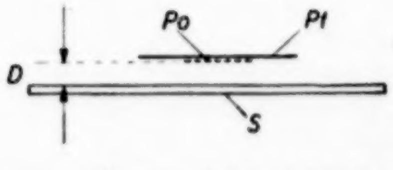

Fig. 1. Schematic outline of arrangement for irradiation. Po is the ^{210}Po alpha source on a platinum disc (Pt). S is the specimen. D indicates the distance between source and specimen.

The counting was continued for 300 ± 2 seconds and the background value for 300 seconds was subtracted. In some cases the pulses were also visualized on a cathod ray oscilloscope and recorded on moving film.

Results obtained at different points of time had to be corrected for ^{210}Po decay to be comparable.

RESULTS

Aluminium foils of 97 per cent purity (84 mg/cm^2) were irradiated and the half-life of the induced radioactivity was measured on impulse records on moving film. Six runs yielded a half-life 2.54 ± 0.08 min. The scintillation spectrum showed a gamma line at 0.5 MeV (positron annihilation) and a beta activity around 3 MeV. These data are consistent with the properties of ^{30}P described by previous authors.

Aluminium foils (84 mg/cm^2) were placed at different distances in air from the ^{210}Po source. The relation between the induced activity and the distance is shown in Fig. 2.

Stacked aluminium foils (2.36 mg/cm^2) were irradiated. Nearly all of the induced activity was found in the top foil, indicating that only a very thin layer on the surface of the specimen was activated. This is consistent with the Q value of the reaction as discussed above.

Aluminium alloys with different percentages of Al were subjected to activation and subsequent counting. In other runs some different powdered Al compounds were activated and counted. The results, corrected for general composition of specimen[6], are plotted in Fig. 3.

Attempts to activate liquid specimens must be stopped because water tended to condense on the polonium source.

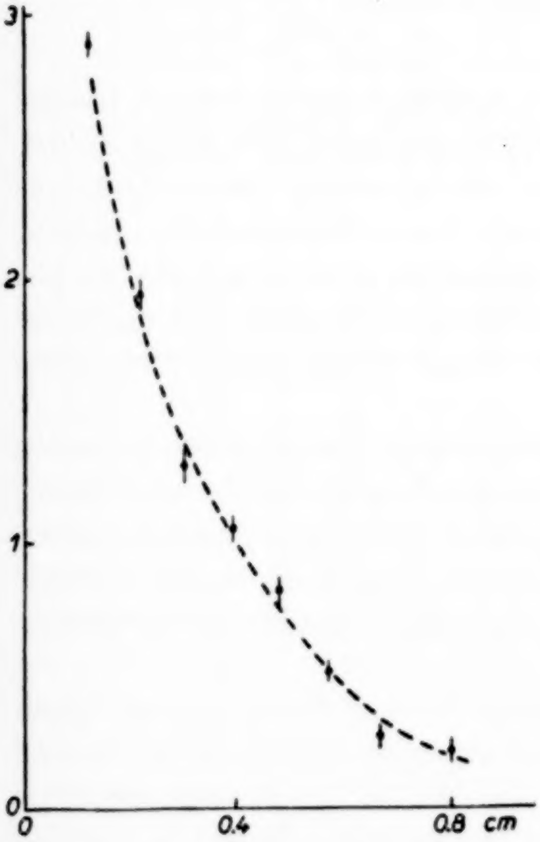

Fig. 2. Relation between accumulated counts (ordinate) and distance D in Fig. 1 (abscissa). Ordinate: counts · 10^3 during 5 minutes. Abscissa: distance in cm.

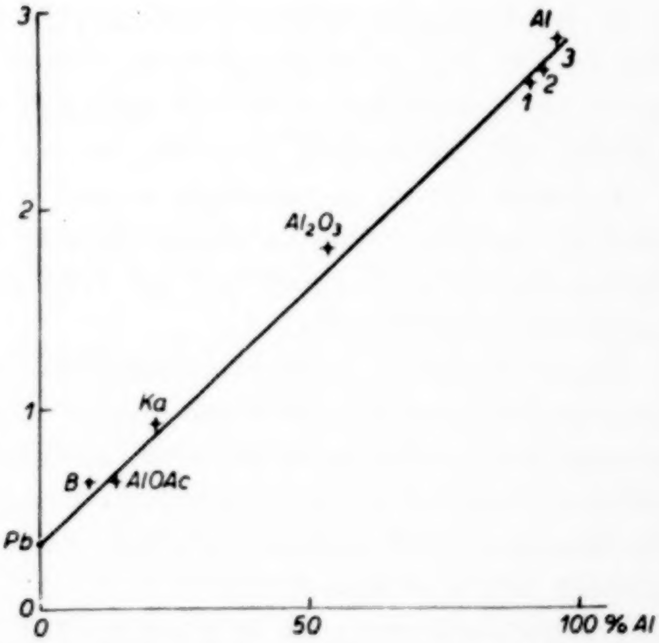

Fig. 3. Relation between Al content in % (abscissa) and accumulated number of counts (including background) during 5 minutes (ordinate) in units of 10^3. Specimens: Pb, lead. B, alloy containing about 90% Cu and 10% Al. AlOAc, aluminium-oxyacetate. Ka, kaolin. Al_2O_3, aluminiumoxide. $Al_{1,2,3}$, aluminium alloys containing 89, 94 and 97% Al respectively, the remainder mainly being copper, zinc and magnesium.

DISCUSSION

The results indicate that there is a relation between the Al content and the obtained number of counts in the Geiger-Müller tube.

Several factors influence the accuracy of the method. As shown in Fig. 2, the activation is extremely sensitive to the *distance between source and specimen*. A change of distance of 0.1 mm corresponds to a change of induced activity of 5 per cent. The *distance between the activated specimen and the Geiger-Müller tube* is also of importance as indicated in Fig. 4. A change of 0.1 mm gave a change in counting rate of about 1 per cent, using our experimental set-up. Special care must therefore be taken to adjust in a reproduceable manner, or measure, the distance between the alpha source and the specimen.

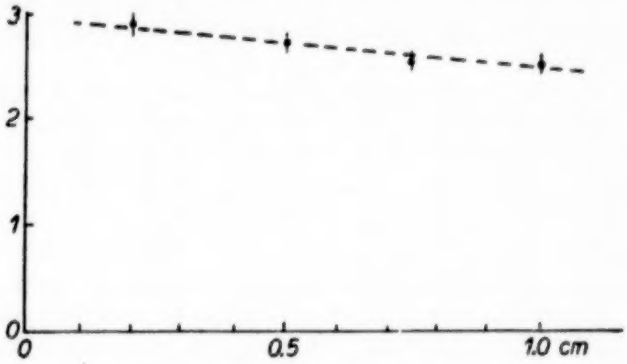

Fig. 4. Influence of distance from Geiger-Müller tube window in cm (abscissa) on accumulated counts in units of 10^3 during 5 minutes (ordinate).

We made some attempts to perform the irradiations in helium gas in order to reduce the energy loss of alpha particles before reaching the specimen. We experienced, however, that ^{210}Po tended to volatilize and infect the specimen and helium gas leaving the irradiation chamber, so we had to stop these experiments quickly.

A *change in time of activation or time of counting* caused an error of about 0.15 per cent per second, while a *change in time interval* between activation and counting caused an error of about 0.5 per cent per second. These errors agree with those estimated theoretically.

The activation is, in addition, sensitive to the *composition in general* of the specimen because the stopping power per mg/cm^2 for alpha particles depends on the elementary composition as discussed by ODEBLAD[6]. Binary samples in which this general composition is expected to vary more regularly with composition appear especially suitable for analysis. Such samples are *e.g.*, Al-Cu alloys, Al_2O_3-H_2O system for chromatography, alum-protein mixtures.

The method proposed here is very rapid and simple. It may have several applications in metallurgy, chemistry, pharmacology and experimental medicine. If used we recommend to check the half-life of the induced activity and its gamma spectrum in order to detect contamination with B and Mg in the samples. Boron is revealed by a 10 minute component in the decay curve, and magnesium by the presence of a 1.8 MeV gamma line in the scintillation spectrum.

The alpha particle beam of a cyclotron can be used instead of a radioactive alpha source. It is then essential to monitor the beam with Al foils irradiated simultaneously. This could be made *e.g.* with a rotating sample holder.

ACKNOWLEDGEMENTS

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SUMMARY

The ^{27}Al (α, n) ^{30}P reaction has been used to detect Al in different specimens. A ^{210}Po alpha source was used. The over-all method error in one determination was about 5 per cent. Binary systems containing Al are expected to be most favorable for analysis.

RÉSUMÉ

La réaction nucléaire ^{27}Al (α, n) ^{30}P a été utilisée pour le dosage de l'aluminium dans différents milieux. On utilise pour cela ^{210}Po comme source de rayons alpha. L'erreur due à la méthode est de 5%. Les systèmes binaires renfermant Al conviennent très bien à l'analyse.

ZUSAMMENFASSUNG

Die Kernreaktion ^{27}Al (α, n) ^{30}P wurde für die Bestimmung von Al in verschiedenen Objekten verwendet. Ein ^{210}Po-Präparat war die Quelle der Alpha-Teilchen. Der Methodenfehler war etwa 5% pro Einzelbestimmung. Binäre Systeme mit Al sind wahrscheinlich die besten analytischen Objekte.

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RADIOACTIVATION ANALYSIS OF ARSENIC IN TUNGSTEN

by

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The presence of trace impurities in tungsten is known to have a marked influence on its metallurgical properties. Therefore it is of great importance to the electric lamp industry to have accurate analytical methods of determining the impurity content of the tungsten used for filaments. It was for this reason that the following investigation was carried out, as it is thought possible that the presence of microgram quantities of arsenic might affect appreciably the properties and behaviour of the metal.

The principles underlying the radioactivation technique are now well known and comprehensive surveys of the scope of the method have been published[1]. Therefore the theory will not be referred to in the following discussion except where it has a direct bearing on the methods used.

When natural tungsten is subjected to irradiation by thermal neutrons, two distinct radioactive species are produced

$$(1)\quad {}^{184}\mathrm{W}\ (n,\gamma)\ {}^{185}\mathrm{W} \xrightarrow{\beta'} {}^{185}\mathrm{Re}\ (t_{\frac{1}{2}} = 73.2 \text{ days})$$

β (MeV)	*γ (MeV)*
0.428	—

$$(2)\quad {}^{186}\mathrm{W}\ (n,\gamma)\ {}^{187}\mathrm{W} \xrightarrow{\beta'+\gamma} {}^{187}\mathrm{Re}\ (t_{\frac{1}{2}} = 24.1 \text{ h})$$

β (MeV)	*γ (MeV)*
1.33 (30%)	0.072
0.63 (70%)	0.134
	0.479
	0.619
	0.686

Of these two reactions, the activity of the second predominates. For example, one week's irradiation of natural tungsten at a flux of 10^{11} neutrons/cm²/sec (Pile factor = 1) produces activities of 310 μc/g and 100 mc/g respectively (Fig. 1).

Any arsenic impurity present will be activated according to the following equation

$$(3)\quad {}^{75}\text{As}\ (\text{n}, \gamma)\ {}^{76}\text{As} \xrightarrow{\beta' + \gamma} {}^{76}\text{Se} \qquad (t_{\frac{1}{2}} = 26.8\ \text{h})$$

β (MeV)	γ (MeV)
3.04 (60%)	1.70
2.49 (25%)	1.2
1.29 (15%)	0.55

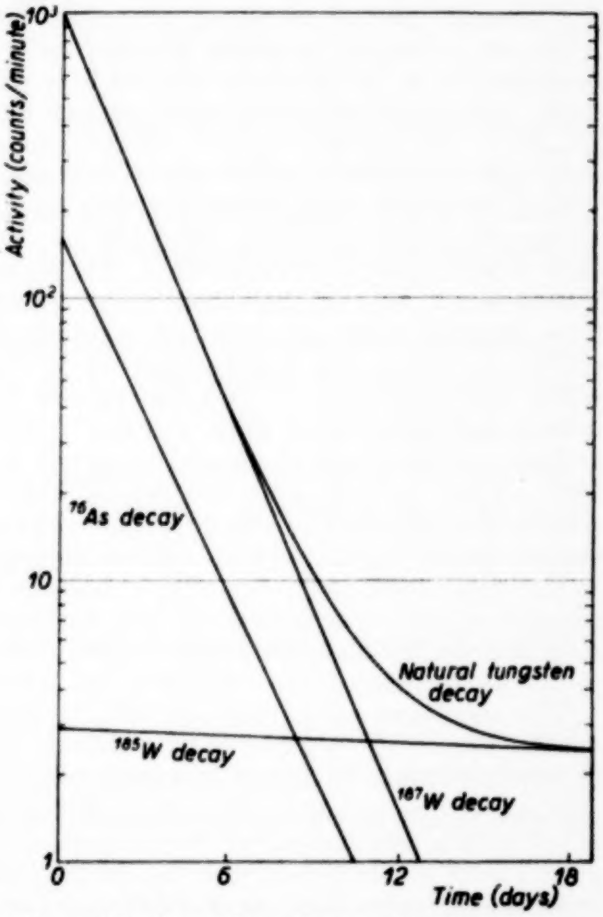

Fig. 1 Radioactive decay of natural tungsten after thermal neutron irradiation, showing similarity to decay of ^{76}As.

The activity produced is 90 mc/g for one week's irradiation at a pile factor of one.

RADIOCHEMICAL PURITY

In cases where the activity of the impurity is very much less than that of the matrix, the purity of the product separated for counting is of the utmost importance. There are three main methods whereby the radiochemical purity of a separation may be estimated: — half life measurements, absorption measurements, and repeated separations in the presence of hold back carrier. Let us consider these for the case of arsenic and tungsten.

(a) *Half life measurements.* Fig. 1 shows the similarity in slope between the arsenic and the tungsten — 187 isotope. It indicates, therefore, that it is only with the utmost difficulty that the purity of separation can be determined in this manner. Measurement of the contamination by allowing the short lived isotopes to decay and then counting the longer lived tungsten — 185 would also be an unreliable method. The final activity produced is only 0.003 times that of the original tungsten, thus giving an impossibly high correction factor on considering the statistical fluctuation of low counting rates.

(b) *Absorption measurement.* Fortunately the maximum beta energies of radioarsenic are appreciably higher than the energies of those emitted by ^{187}W (equations 2 and 3), and so some measure of the arsenic purity can be obtained by this method. Accurate measurements, however, are greatly hindered by the presence of the intense gamma background, so that this technique is of little use for quantitative estimations.

(c) *Repeated separations.* In this method, the arsenic is repeatedly separated in the presence of tungsten hold back carrier until constant values are obtained for the original arsenic concentration. The efficiency of this technique is independent of the energies of the radiations and of the half lives, and so has none of the limitations of the previous two. This is the method we have adopted, although energy measurements have been taken as an added safeguard.

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Chemical separation of arsenic

The method we finally adopted for the determination of arsenic in tungsten is similar in many respects to that which we have given in connection with the determination of arsenic in silicon[2]. The method, described in the following paragraphs, was developed as a result of preliminary experiments details of which are given later.

About 50 mg of tungsten powder were sealed in a silica ampoule and subjected to thermal neutrons for a week in the pile at Harwell. An ampoule containing 10 to 20 mg of arsenious oxide was simultaneously irradiated to act as a standard. On return, the ampoule containing tungsten was cracked open and the contents carefully transferred to a potassium hydroxide hydrogen peroxide mixture which contained 60 mg of arsenious oxide as carrier.

The flask was warmed on a water bath until solution of the tungsten was complete (about 30 minutes), when it was attached to a distillation apparatus and the contents taken to low bulk under oxidizing conditions. The distillate was discarded and the solution acidified with hydrochloric acid in the presence of hydrogen peroxide and again taken to a small volume. This distillate was also discarded and hydrobromic acid added to the remaining liquid. The reduced solution was distilled as before, with the condenser delivery tube dipping below distilled water in the receiver. In this distillation, arsenic came over as the volatile trichloride which was hydrolysed on contact with water.

The apparatus was thoroughly cleaned, both with distilled water and with solutions of tungsten and arsenic carrier, until no radioactive contamination was detectable. The arsenic solution was then redistilled in the presence of precipitated inactive tungstic oxide in the manner described above. A solution of sodium tungstate complexed with excess tartaric acid was added to this final distillate to act as hold back carrier, and the whole, after addition of solid ammonium hypophosphite, was boiled for half an hour to coagulate the precipitated arsenic. The precipitate was centrifuged off, washed well with distilled water, transferred to a counting tray, dried under an infrared lamp, weighed and counted.

The arsenious oxide standard was treated as follows. The ampoule was cracked open and the contents carefully washed into a caustic potash-peroxide solution containing a known amount of about 100 mg of dissolved arsenious oxide. On complete solution, the liquid was made up to 100 ml. A one millilitre sample of this was diluted a hundred-fold in the presence of a further 100 mg of arsenious oxide. An aliquot of this final solution was taken (the amount required to give a reasonable count may be roughly calculated assuming the pile factor and the geometry of the counting system) and added to an alkaline peroxide solution containing 60 mg of arsenious oxide.The arsenic was precipitated after boiling and acidifying with hydrochloric acid by the method given above, and finally dried, weighed and counted. The presence of inactive arsenious oxide during the dilution stage was to minimize errors incurred by absorption on the walls of the vessels. Allowance must be made for the weight contribution of these additions on the final precipitate when calculating the chemical yield.

EXPERIMENTAL

Experiments were conducted to determine the least number of distillations to provide an arsenic precipitate free from radio-chemical contamination. A typical experiment is given below.

39 mg of tungsten powder were irradiated in a silica ampoule for one week at a pile factor of 13 ($1.3 \cdot 10^{12}$ neutrons/cm^2/sec). The tungsten was dissolved with added carrier and the arsenic distilled over as described. This distillate was diluted to 100 ml and divided into two equal parts, A and B. The arsenic in portion A was precipitated and counted (sample 1A, Table I). Hydrogen peroxide was used to re-dissolve the arsenic, and the resulting solution was redistilled, precipitated and counted (sample 2A).

Portion B was redistilled without first precipitating, and the arsenic activity determined (sample 2B). As the activity in this case corresponded to an impurity concentration very similar to that obtained from sample 2A, the two arsenic precipitates were re-dissolved in peroxide and the solutions combined. Further distillations and precipitations were carried out and the successive activities determined (samples 3 and 4, Table I).

TABLE I

Number of distillations	*As concentration (ppm)*
1A	25.0
2A	9.2
2B	10.7
3	11.1
4	10.4

The counts obtained in this way were related to the original arsenic concentration in tungsten by reference to an arsenious oxide standard, and the identity of the activity on the final arsenic precipitate was checked by energy and half life measurements. The complete results are given in Table I.

DISCUSSION

It can be seen that, within experimental error, the last four arsenic concentration values are constant, indicating that removal of contaminating impurities is complete at the second distillation stage. Thus, the necessity of more than two distillations to obtain a radiochemically pure arsenic precipitate is eliminated. The first distillation, however, gives a high result, and in earlier experiments we have obtained *apparent* values of up to 200 ppm in the first distillate. We believe that these higher contamination figures were due to distilling the reduced solution to too low a bulk.

The rather low figure for sample 2 A coincided with a low yield of arsenic and so probably has no significance. Its agreement with the value obtained from sample 2B seems to show that precipitation of the arsenic in the presence of hold back carrier after the initial distillation and redissolution is an unnecessary purification stage and may be omitted.

A simple calculation may be performed to determine the purification factor per distillation.

As the specific activities and the half-lives of arsenic and tungsten 187 are very similar, then we may say as a first approximation that x ppm of arsenic would produce the same activity as x ppm of tungsten. If we now take our most highly contaminated arsenic figure after one distillation (200 ppm) and assume the arsenic contribution to the total activity is negligible, then the tungsten contamination would also be 200 ppm and therefore the separation factor at worst would be $2 \cdot 10^{-4}$ per distillation. From this, one can see that a second distillation with hold-back carrier should reduce the tungsten contamination down to an insignificant level.

ACKNOWLEDGEMENTS

The authors express indebtedness for the encouragement and assistance in this work to colleagues in the Research Laboratory and other departments of the BTH Company.

SUMMARY

A radioactivation method has been devised for the determination of arsenic impurity in tungsten powder. Investigations to determine the minimum number of distillations required for radiochemical purity are described.

RÉSUMÉ

Une méthode par radioactivation a été élaborée pour le dosage de l'arsenic (à l'état d'impureté) dans une poudre de tungstène. Les recherches effectuées pour la détermination du nombre minimum de distillations nécessaires pour l'obtention d'une pureté radiochimique sont décrites.

ZUSAMMENFASSUNG

Eine Radioaktivierungsmethode zur Bestimmung des Arsens, welches als Verunreinigung in Wolframpulver vorkommt, wurde ausgearbeitet. Die Untersuchungen werden beschrieben, welche ausgeführt wurden, um die zur Erreichung radiochemischer Reinheit minimal erforderliche Anzahl Destillationen festzustellen.

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PAPER CHROMATOGRAPHY OF INORGANIC IONS
XIV. SEPARATION OF GADOLINIUM GROUP RARE EARTHS

by

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INTRODUCTION

In the last part of this series (Part XIII[1]) we have indicated the behaviour of the rare earths in polar solvent mixtures containing HCl. Good separations of several mixtures are possible in the solvents there described but no mixtures of adjacent rare earth elements could be resolved with the exception of some pairs such as La-Ce and Er-Tm. Complexation of rare earths in a weakly acid medium cannot be used for separations on a tracer scale as has been discussed previously[2]. Thus it was decided to study the effect of additions, known to produce complexes with rare earths, to one of the polar solvents studied[1] namely ethanol containing 10% 2*N* HCl.

Of the complexants listed below, we found that only thiocyanate ions could change the sequence from that of the ionized rare earths. An optimum concentration of thiocyanate yields a sequence which appears to be composed of the sequence of the hydrated ions and the degree of complexation. Since the movement of the yttrium rare earths decreases with increasing atomic number, no separation was achieved in this region, while in the region from Nd-Tb, a constant R_F difference greater than that recorded for the ionized elements permits a separation of adjacent rare earths with a development of only 48 hours.

EXPERIMENTAL

The following solvents were tried with ascending development overnight and a series of rare earth chlorides:

Solvent	*Ions tested*	*Remarks*
Ethanol 85 ml Acetylacetone 5 ml 2*N* HCl 10 ml	La, Y, Pr, Sm, Tb, Dy, Ho, Er and Lu.	R_F values are the same as with ethanol 90 ml, 2*N* HCl 10 ml
Ethanol 85 ml Tributyl phosphate 5 ml 2*N* HCl 10 ml	,,	,,
Ethanol 85 ml Ethyl acetoacetate 5 ml 2*N* HCl 10 ml	,,	,,
Ethanol 80 ml Acetic acid 10 ml 2*N* HCl 10 ml	,,	,,

We have previously noted[2] that in propanol-HCl mixtures containing 5% NH_4CNS all rare earths move with the liquid front. Thus it was decided to try varying the amounts of NH_4CNS added to the mixture ethanol-10% $2N$ HCl. Fig. 1 shows the variation in R_F values when increasing the NH_4CNS concentration from 0.01% to 2% for a number of rare earth ions.

The maximum R_F differences in the gadolinium group occur in the region of 1% NH_4CNS. The yttrium earths do not separate as the additive effects of hydration and complexation tend

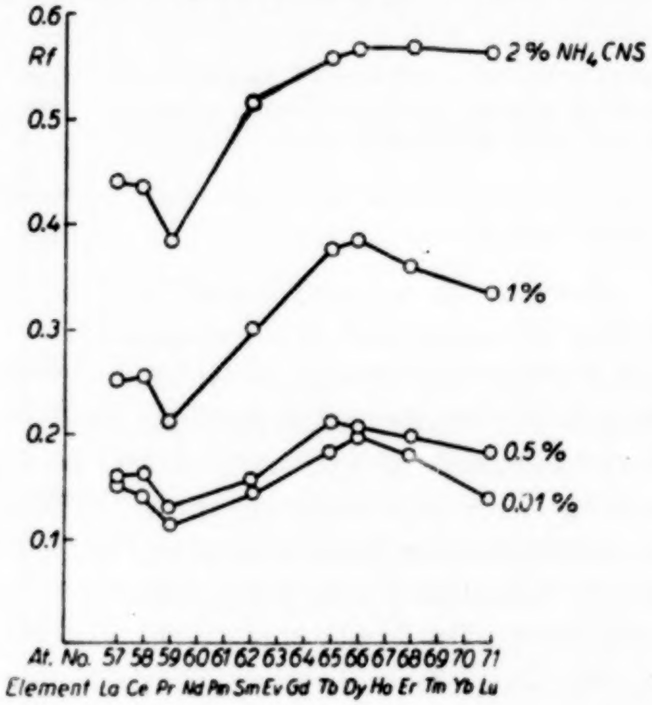

Fig. 1. Variation of R_F values of rare earth chlorides with increasing amounts of NH_4CNS in ethanol-10% $2N$ HCl.

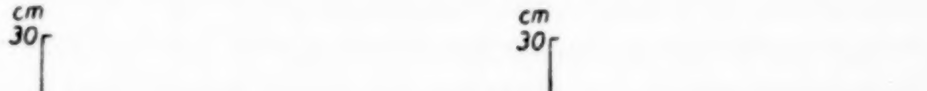

Fig. 2. The movement of Pr, Nd, Sm, Eu, Gd and Tb when developed for 48 hours with ethanol 90 ml, $2N$ HCl 10 ml, NH_4CNS 1 g. The spots are revealed with ammoniacal alcoholic hydroxyquinoline.

to diminish any differences previously noted. With a simple development it is thus possible to separate the mixture Nd-Sm-Tb into three distinct spots. All spots are detected with ammoniacal alcoholic hydroxyquinoline as described in the previous communication. Separation or near separation of adjacent rare earths may be obtained by descending development over longer time. Fig. 2 shows the movement of the elements 60-65 with 48 hours descending development and Fig. 3 the separation of several artificial mixtures. In the region of the gadolinium earths this is the best separation so far recorded by paper chromatographic and electrophoretic methods.

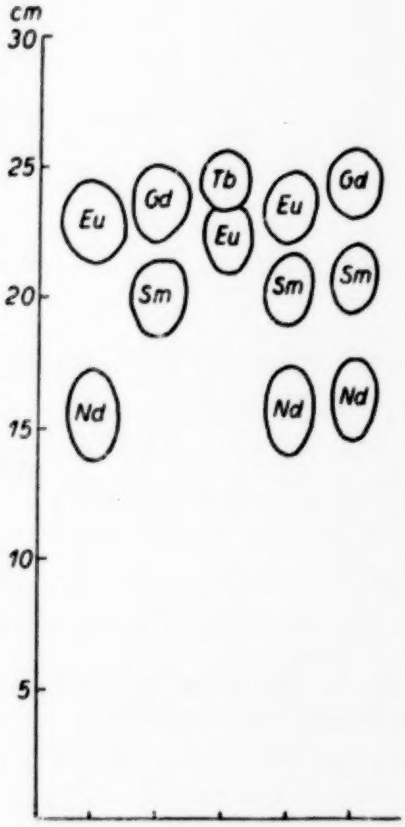

Fig. 3. Separation of several artificial mixtures of gadolinium rare earths. The samples were applied with capillaries as thin lines 2 cm long. Solvent and reagent as in Fig. 2.

DISCUSSION

The effect of an addition of a complexant to ethanol-10% 2*N* HCl may be considered as a measure of the degree of complex formation at the pH of the solvent. Thus according to our results acetylacetone, tributyl phosphate, ethyl acetoacetate and acetic acid do not produce complexes with rare earths in dilute HCl. With thiocyanate the transition from completely dissociated to completely complexed ions lies in the region of 0.5%-2% NH_4CNS for the higher rare earths. The solvent containing 1% NH_4CNS does not separate the yttrium earths as mentioned above. Since the factors influencing the movement of the ions are not only acidity and CNS concentration but also the H_2O concentration, it is likely that mixtures of lower polarity may yield better separation effects for the yttrium group. Preliminary experiments in this direction with acetone instead of alcohol yielded comets but no noticeable improvement in the separation.

SUMMARY

The gadolinium group rare earths were separated by paper chromatography using ethanol 90 (ml), 2*N* HCl (10 ml) and NH_4CNS (1 g) as solvent. Complete separation of the mixture Nd-Sm-Eu was achieved. The spots of Eu-Gd-Tb overlap slightly, but Eu may be separated well from Tb.

RÉSUMÉ

Les terres rares du groupe du gadolinium peuvent être séparées par chromatographie sur papier, en utilisant comme solvant 90 ml d'éthanol, 10 ml d'HCl 2*N* et 1 g de NH_4SCN. Une séparation complète est obtenue avec le mélange Nd-Sm-Eu. Les taches formées avec le mélange Eu-Gd-Tb chevauchent partiellement, mais Eu peut être séparé facilement de Tb.

ZUSAMMENFASSUNG

Die seltenen Erden der Gadolinium-Gruppe können papierchromatographisch unter Verwendung von Äthanol (90 ml), 2*N* HCl (10 ml) und NH_4CNS (1 g) als Lösungsmittel getrennt werden. Das Gemisch Nd-Sm-Eu konnte vollständig getrennt werden. Die Flecke des Gemisches Eu-Gd-Tb überdecken einander teilweise, aber Eu konnte gut von Tb getrennt werden.

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THE CHROMATOGRAPHY OF SOME HYDRAZINE DERIVATIVES ON PAPER

by

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In the course of studies on the alkyl- and acylhydrazines[1], paper chromatography afforded a convenient method for their detection and identification. It was particularly useful for determining the degree of completion of certain reductions of acylhydrazines by lithium aluminum hydride which were of long duration (24-72 hours). A sample of the reaction mixture was chromatographed on a circular piece of filter paper, and within an hour a rough estimate of the relative proportions of starting material and product could be made from the intensities of the bands. SATAKE AND SEKI, in a study of the chromatography of monoacylhydrazines on paper (ascending method), used a detecting spray of *n*-butyl alcohol saturated with 10% ammoniacal silver nitrate[2]. They found that the best solvent systems consisted of *iso*amyl alcohol, water, and a heterocyclic base, such as a lutidine or collidine. In the present work the preferred solvent system was *n*-butyl or *iso*amyl alcohol, water, and acetic acid. The hydrazine derivatives were generally detected by spraying the chromatograms with Ehrlich's reagent[3] (an ethanolic solution of *p*-dimethylaminobenzaldehyde hydrochloride), or with ammoniacal silver nitrate, or with a solution of ninhydrin in acetone.

EXPERIMENTAL

Materials

Hydrazine derivatives were purchased or were prepared by known methods, the references for which are cited in Table I.
Ehrlich's reagent[3] was prepared by dissolving 50 mg of *p*-dimethylaminobenzaldehyde in 100 ml of absolute ethanol containing 1 ml of conc. hydrochloric acid.
Ammoniacal silver nitrate was prepared from equal volumes of 5*N* ammonium hydroxide and 0.1*N* aqueous silver nitrate.
Filter paper, Whatman No. 1, in sheets and size No. 9 disks.
n-Butyl alcohol and *isoamyl alcohol*, Fischer, certified grade, used without further purification.
Acetic acid, Du Pont, used without further purification.

General procedures

(a) *Circular paper chromatography.* The procedure was adapted from that described by BLOCK[4]. The solvent system, composed of the upper layer from a mixture of *n*-butyl alcohol, acetic acid, and water in the volume proportions of 4 : 1 : 5, or the upper layer from a mixture of *iso*amyl alcohol, acetic acid and water in the volume proportions of 10 : 1.5 : 10, was allowed to equilibrate for two hours in a covered Petri dish. The filter paper disk was prepared by marking the exact center with a pencil dot and cutting a wick of 3-4 mm diameter from the disk. A dilute solution of the hydrazine derivative in a volatile solvent such as methanol was prepared and an aliquot containing 10-20 mg of the hydrazine derivative was applied with a melting point capillary to

TABLE I

R_F VALUES OF SOME HYDRAZINE DERIVATIVES

Compound	*Reference*	*Isoamyl alc. acetic acid H_2O circular*	*1-Butanol, acetic acid, H_2O*		*Detecting agents*	
			circular	*ascending*	*$[Ag(NH_3)_2]^+$*	*Ehrlich's reagent*
1,2-Diformylhydrazine	6	0.26			+	+
1,2-Diacetylhydrazine	6	0.48			+	+
1,2-Dipropionylhydrazine	7	0.81			+	+
1,2-Dibutyrylhydrazine	8	0.91			—	+
1,2-Dibenzoylhydrazine	9	—			—	—
1,2-Diformyl-1,2-dimethylhydrazine	10	0.60			—	+
1,2-Diacetyl-1,2-dimethylhydrazine	1	0.74			—	+
1-Formyl-2,2-dimethylhydrazine	a	0.72			+	+
1-Acetyl-2,2-dimethylhydrazine	1	0.76			+	+
1-Benzoyl-2,2-dimethylhydrazine	1	0.88			+	+
Hydrazine dihydrochloride	b	0.00	0.39	0.16	+	+
Methylhydrazine sulfate	b	0.13	0.47	0.17	+	+
1,1-Dimethylhydrazine hydrochloride	b	0.29	0.53	0.20	+	+
1,2-Dimethylhydrazine dihydrochloride	1	0.27	0.57	0.23	+	+
Trimethylhydrazine hydrochloride	11	—	0.42	0.23	+	+
1,2-Diethylhydrazine dihydrochloride	1	0.30	0.55	0.25	+	+
Ammonium chloride	b		0.33		+	+
Methylamine hydrochloride	b		0.38		+	+
Dimethylamine hydrochloride	b		0.41		+	+

a) Prepared by refluxing 1,1-dimethylhydrazine with an excess of ethyl formate.
b) Obtained commercially.

the marked center of the disk, leaving a wet spot with a diameter of not more than 6 mm. After the solvent had evaporated, the disk was placed in the Petri dish, with the wick in the solvent, and covered. Development of the solvents to the limits of the paper at the temperatures used (24-28°) required about two hours, but adequate separation was effected within one hour. After the solvents had been removed by drying in an oven at 40-50°, the chromatogram was sprayed with the appropriate solution to detect the hydrazine derivatives. Chromatograms sprayed with Ehrlich's reagent were dried for about ten minutes at 90-95°, and when viewed under an ultraviolet light, the location of the acylhydrazine was revealed by a fluorescent orange band. After several hours the orange bands became visible in white light. Occasionally the bands were visible in white light directly after spraying. This was usually an indication that too much sample had been used in which case the bands were thick and the *R_F* values were unreliable. Chromatograms sprayed with ammoniacal silver nitrate were dried at 40-50° until a brown or black ring appeared (usually 30-90 minutes). The *R_F* values were determined in the usual way. Somewhat more consistent results were obtained using the method of SAIFER AND ORESKES[5] to reduce evaporation of the solvents, but usually the simpler method described above was adequate. The narrowest and most clearly defined bands were found when the solvent system was fresh (not more than one day old). The observation made by SAIFER AND ORESKES that the distance between the solvent surface and the paper disk has a marked affect on the *R_F* values was confirmed. For reproducible results the solvent level in the Petri dish was adjusted to a distance of about one cm from the paper before each run.

(b) *Ascending method.* The solvent system was allowed to equilibrate for several hours in the bottom of a Pyrex cylinder covered by a glass plate. The paper strips were prepared by applying solutions of the hydrazine derivatives, prepared as described in (a), at 2 cm intervals along a base line 3 cm from one end of the paper strip. The paper strips were supported on a glass hook held in a rubber bung which was inserted in a hole cut in the glass cover plate. The strips were allowed to equilibrate with the vapors in the cylinder for two hours after which they were lowered into the solvent. For a paper strip six inches wide about sixteen hours was required for the solvent front to reach a height of 30 cm. Equilibration and ascent of solvent occurred at temperatures of 18-20°. The solvents were removed by drying in an oven at 40-50°. The chromatograms were sprayed as described in part (a) and the R_F values determined.

RESULTS AND DISCUSSION

Although circular paper chromatography was generally used for convenience, for absolute identification the ascending method was preferred, since a known sample could be run beside the unknown. Results of both types are shown in Table I, in which the R_F values are the averages of several runs. The average deviation was about $\pm$ 0.05 for any R_F. Ammonium chloride and its methyl and ethyl homologs are included for comparison.

Of the two detecting agents described, Ehrlich's reagent was generally more satisfactory since it is considerably more sensitive than ammoniacal silver nitrate. Thus 5-6 μg of 1,2-diacetylhydrazine could be detected with Ehrlich's reagent, whereas 15-20 μg were required with ammoniacal silver nitrate. In addition, Ehrlich's reagent gives positive tests with a wider variety of hydrazine derivatives. Thus, monoacylhydrazines, 1-acyl-2,2-dimethylhydrazines, and 1,2-diacylhydrazines could be detected with Ehrlich's reagent. 1,2-Diformyl-1,2-dimethylhydrazine and 1,2-diacetyl-1,2-dimethylhydrazine also gave positive tests, but 1,2-dibenzoyl-1,2-dimethylhydrazine could not be detected by this method. It is likely that the smaller acyl groups are hydrolyzed by the acidic detecting agent to the dialkylhydrazines, which give the positive test. The benzoyl groups would not be expected to undergo hydrolysis as readily.

Ammoniacal silver nitrate was satisfactory for monoacylhydrazines and for 1,2-diacylhydrazines of low molecular weight, but negative results were obtained with diacylhydrazines of higher molecular weight. As an alternative detecting agent the use of a 0.2% solution of ninhydrin in acetone was examined, but negative tests were obtained with 1,2-diacylhydrazines, even when the chromatograms were first sprayed with a 5% solution of trichloroacetic acid in 95% ethanol and dried at 90-95° in an attempt to effect hydrolysis of the acyl groups. Neither ninhydrin nor ammoniacal silver nitrate gave positive tests with 1,2-diacyl-1,2-dimethylhydrazines. With mono-, di-, and trialkylhydrazines all three means of detection could be used, but Ehrlich's reagent was generally the most convenient and was considerably more sensitive than was ammoniacal silver nitrate solution.

The most satisfactory solvent system for acylhydrazines was the upper layer from a mixture of *iso*amyl alcohol, acetic acid, and water in the volume proportions of 10 : 1.5 : 10. When 1-butanol was substituted for *iso*amyl alcohol the diacylhydrazines were found at the solvent front. On the other hand, the upper layer from a 1-butanol, water, and acetic acid mixture (4 : 5 : 1) was more satisfactory for the identification of the simple alkylhydrazines (in the form of their hydrochlorides or sulfates).

Examination of Table I reveals that as the organic residue of the acyl- or alkylhydrazine is increased in size, the R_F also increases, a correlation which is well-known[12]. The large difference in R_F values obtained by the circular method on the one hand and the ascending technique on the other, using the *n*-butyl alcohol system for both, can be accounted for in several ways. The fact that the two techniques were used at temperatures differing by 5-10° is the most obvious reason. In addition, it

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has been observed that the greater the distance between the point of contact of the solvent with the paper and the point of application (starting point) of the sample, the smaller the R_F values will be[13]. A similar observation has been reported in a study of circular paper chromatography[5], in which the larger the distance between the solvent surface and the filter paper disk, the smaller are the R_F values. In the present study the distance between the solvent and the paper in the circular chromatography was about one cm while the distance in the ascending method was 3 cm from the solvent to the point of application of the sample. Therefore, higher R_F values would be expected for the samples run on circular chromatograms.

SUMMARY

A study is described of the chromatography on paper of some alkylhydrazines and some mono- and diacylhydrazines by both the circular and ascending methods. For the acylhydrazines the solvent system preferred was the upper layer from isoamyl alcohol, acetic acid, and water in the volume proportions of 10 : 1.5 : 10 respectively. The upper layer from a mixture of *n*-butyl alcohol, acetic acid, and water in the volume proportions of 4 : 1 : 5 respectively, was preferred for the alkylhydrazines. For detection of the hydrazine derivatives on the chromatogram a spray of *p*-dimethylaminobenzaldehyde hydrochloride in ethanol (Ehrlich's reagent) was most satisfactory, although ammoniacal silver nitrate or ninhydrin could be used in some cases.

RÉSUMÉ

L'auteur a étudié la chromatographie sur papier de quelques hydrazines alcoylées et de quelques hydrazines mono- et diacylées, au moyen des techniques dites ascendante et circulaire. Pour les hydrazines acylées, le système de solvants choisi a été la couche supérieure du mélange alcool *iso*amylique, acide acétique et eau dans les proportions (en volumes) 10 : 1.5 : 10 respectivement. La couche supérieure d'un mélange alcool *n*-butylique, acide acétique et eau en proportions 4 : 1 : 5 respectivement a été trouvée préférable pour les hydrazines alcoylées. Pour la détection des dérivés de l'hydrazine sur le chromatogramme, le chlorhydrate de *p*-diméthylaminobenzaldéhyde dans l'alcool éthylique (réactif d'Ehrlich) s'est montré le réactif le plus satisfaisant, bien que le nitrate d'argent ammoniacal et la ninhydrine puissent être utilisés dans certains cas.

ZUSAMMENFASSUNG

Die Papierchromatographie einiger Alkylhydrazine, sowie einiger Mono- und Diacylhydrazine wurde nach der sogenannten „Zirkularmethode" und der „aufsteigenden Methode" untersucht. Für die Acylhydrazine war das beste Lösungsmittelsystem die oberste Schichte eines Gemisches von *Iso*amylalkohol, Essigsäure und Wasser im Volumverhältnis 10 : 1.5 : 10. Für die Alkylhydrazine war die oberste Schichte eines Gemisches von *n*-Butylalkohol, Essigsäure und Wasser im Volumverhältnis 4 : 1 : 5 vorzuziehen. Als Entwickler der Hydrazinderivate auf dem Chromatogramm war *p*-Dimethylaminobenzaldehyd in Äthanol (Ehrlich-Reagenz) am geeignetsten, obwohl auch ammoniakalisches Silbernitrat und Ninhydrin in manchen Fällen benützt werden konnten.

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A STUDY OF THE CONDITIONS FOR THE FORMATION OF NIOBIUM THIOCYANATE

by

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I. INTRODUCTION

The coloured complex formed by niobium with thiocyanate ions has assumed importance in analytical chemistry because of the recent need to analyse ores and minerals for small amounts of this element. A comprehensive investigation of the niobium thiocyanate system has been carried out in recent times by FREUND AND LEVITT[1] and they recommended the following optimum solution conditions for the formation of the thiocyanate complex —2.2M HCl, 0.6M KCNS, 0.04M $SnCl_2$ and 20% acetone. The acetone is included in the solution to intensify the niobium colour, whilst the stannous chloride simply prevents interference from traces of ferric iron. These workers studied the dependence of the absorbancy of the niobium-thiocyanate complex on the concentration of the various reagents by varying the concentration of one reagent at a time whilst keeping the other reagents at suitable fixed values. It was shown that the absorbancy at 385 mμ is critically dependent on the acidity, thiocyanate, acetone and salt concentration. The absorbancy increases with increase in hydrochloric acid concentration and at high concentrations trouble is experienced from the precipitation of potassium chloride. Similarly greater absorbancies are obtained for increases in the thiocyanate and in the acetone contents. Experimental evidence is also given to show that sulphate and tartrate ions affect the absorption. In this work, FREUND AND LEVITT reported that high temperature and high acidity resulted in polymerization of the thiocyanate ions which critically affected the absorption by the blanks at wavelengths less than 360 mμ and to a minor extent at 385 mμ. Thus an increase in absorbancy with time was shown by reagent blank solutions.

In other work LAUW-ZECHA and co-workers[2] extracted the niobium thiocyanate complex into diethyl ether before taking absorbancy measurements. They studied a wide range of acidity and, at the concentration of potassium thiocyanate used (0.75M) maximum absorption was attained when the aqueous phase was 4M in hydrochloric acid. A higher concentration of stannous chloride (0.17M) was used in this work since with concentrations less than 0.05M abnormally high absorbancies were obtained in the presence of niobium (0.732 μg/ml). The extensive decrease in the blank absorptions on extracting with ether can almost certainly be associated with the stannous chloride and polymerized thiocyanate remaining behind in the aqueous phase. Under these conditions, however, the absorbancy of the niobium complex is still critically dependent on the thiocyanate concentration, but almost unaffected by amounts of tartaric acid up to $0.5M$.

In the development of methods for the determination of niobium in ores and minerals, MARZYS[3] examined both the acetone and the ether extraction procedures. With the former procedure he especially emphasizes the necessity for accurate measurement of thiocyanate, hydrochloric acid and acetone additions and recommends that the order of the additions should be as follows — sample aliquot, stannous chloride in hydrochloric acid, thiocyanate in acetone using a freshly-prepared solution 50% v/v in acetone and $1.5M$ in potassium thiocyanate. The solution conditions employed are the same as given by FREUND AND LEVITT, excepting that the stannous chloride concentration has been increased from 0.04 to $0.088M$. Further evidence is given of the instability of the solutions at wavelengths less than 380 mμ. Several modifications are also given to avoid the interference by some elements and to correct for the interferences by others.

All the above workers showed that many other elements caused interference under the conditions for the formation of the niobium thiocyanate complex. These included Ti, V, W, Mo, U, Fe and Ta and the extent of the interference was found to vary appreciably with the solution conditions employed. This variation is understandable since slight changes in solution conditions critically affect the degree of complexation of the interfering metals in different ways. For example, the interference values given by MARZYS for tungsten and vanadium in acetone media are five to ten fold greater than those given by FREUND AND LEVITT, presumably due to the increase in the stannous chloride concentration. Similarly, in LAUW-ZECHA's work there is no interference from uranium for ratios of uranium to niobium of 10 : 1 when the solution contains tartaric acid, whereas molybdenum under the same conditions causes interference. In the absence of tartaric acid, however, uranium interferes and molybdenum does not. This variation in behaviour means that any technique for correcting for the interference of other elements must be very carefully checked for reliability.

From practical experience in using the niobium thiocyanate complex (FREUND AND LEVITT's conditions) for the determination of the niobium content of ores and minerals, it soon became apparent that the careful controls needed to obtain reliable niobium results were time consuming. Final solution conditions were required such that the absorbancy due to the niobium thiocyanate complex was not so critically influenced by the reagent concentrations. It was considered that better information could be obtained on this system by varying the concentration of one of the reagents at different levels of a second reagent. By this means the FREUND-LEVITT conditions have been improved and final solution conditions have been developed for the production of a stable niobium-thiocyanate complex. Full details are given in this paper together with information for reagent blank solutions.

2. EXPERIMENTAL

2.1 The function of stannous chloride in the determination of niobium by its thiocyanate complex

(a) Experiments in the absence of niobium

The preliminary experiments were designed to obtain information on the function of stannous chloride in the niobium determination, since it was felt that the contribution of this reagent

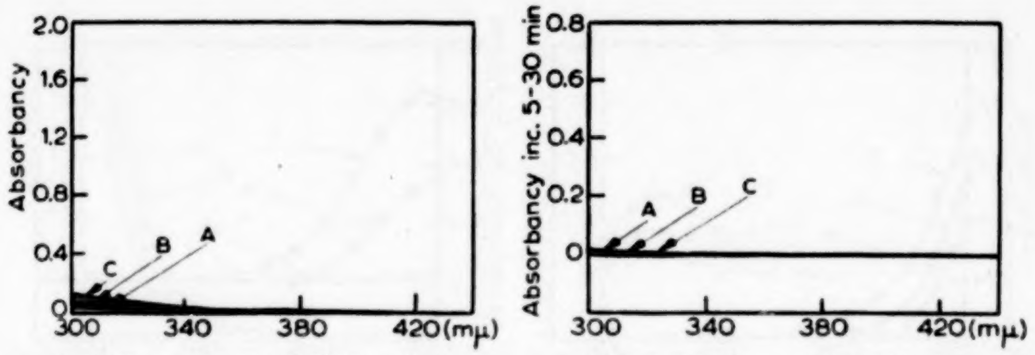

Fig. 1. Acidified 0.06*M* KCNS solutions; A 2.3*M* HCl, B 4.0*M* HCl, C 5.9*M* HCl.
a) Absorption graph (5 min readings). *b*) Stability (absorbancy increase 5-30 min).

was more than simply preventing the formation of the ferric thiocyanate complex. Variations of the absorbancy with wavelength for hydrochloric acid solutions (2.3, 4.0 and 5.9*M*) are shown in Fig. 1 and 2 for potassium thiocyanate concentrations of 0.06*M* and 0.24*M* respectively; stannous chloride being absent from solution in all cases. It is clear from these graphs that the stability of the solutions over a period of 30 minutes decreases with increase in both the thiocyanate and acid concentrations. Moreover there is a definite peak at a wavelength of about 340 mμ for the highest acidity at the 0.24*M* potassium thiocyanate concentration. Absorbancy measurements were obtained with a Beckman spectrophotometer, using 1 cm cells.

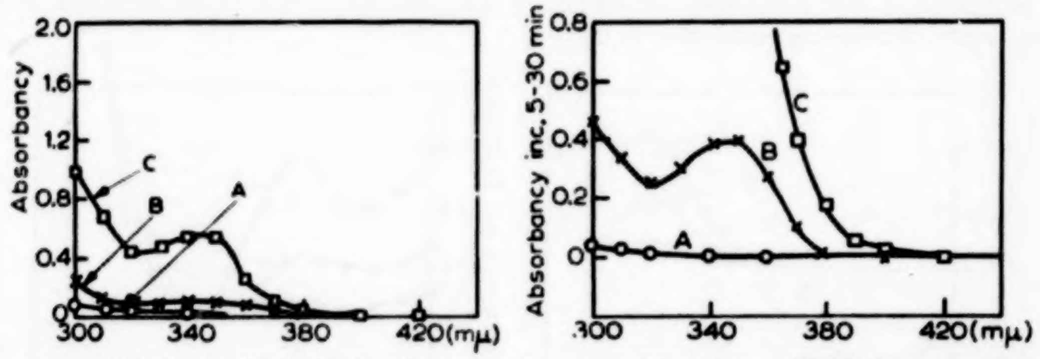

Fig. 2. Acidified 0.24*M* KCNS solutions; A 2.3*M* HCl, B 4.0*M* HCl, C 5.9*M* HCl.
a) Absorption graph (5 min readings). *b*) Stability (absorbancy increase 5-30 min).

In studying the effects of stannous chloride, small concentrations (0.01 and 0.02*M*) were included in hydrochloric acid solutions of increasing strengths (2.3, 3.6 and 7.6*M* respectively) and the resulting absorption spectra are shown in Fig. 3. Although there was negligible absorption of light under these conditions for wavelengths of 340 mμ and higher (Fig. 3a), large increases in the stannous chloride concentration will result in the absorbancy spreading to higher wavelengths (Fig. 3b). These solutions were perfectly stable. On including stannous chloride with HCl-KCNS solutions similar to those used in the construction of Fig. 2, a marked improve-

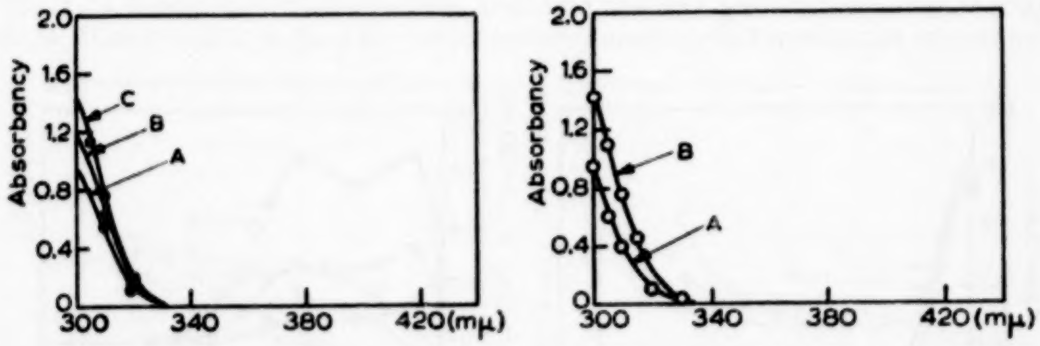

Fig. 3. Absorption graphs for stannous chloride.

a) $SnCl_2$ 0.02*M* (solutions stable)
acidity varied:
A 2.3*M* HCl
B 3.6*M* HCl
C 7.6*M* HCl.

b) HCl 7.6*M* (solutions stable)
$SnCl_2$ varied:
A 0.01*M* $SnCl_2$
B 0.02*M* $SnCl_2$.

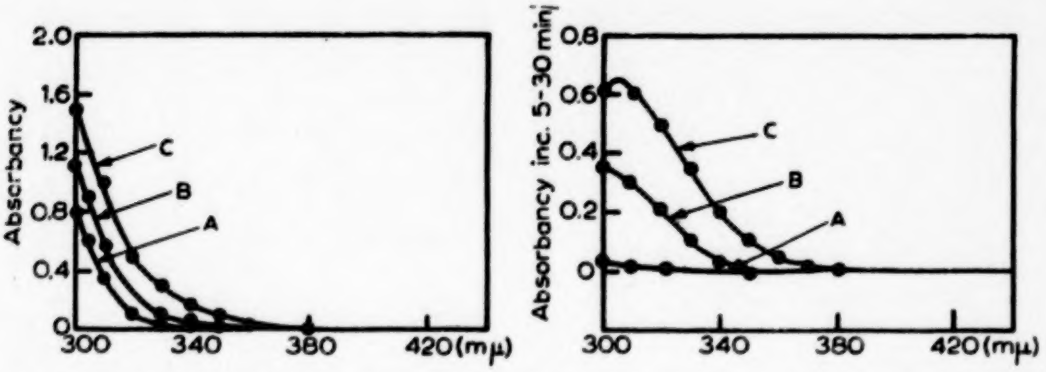

Fig. 4. Stabilizing of acidified 0.24*M* KCNS solutions by 0.01*M* stannous chloride; A 2.3*M* HCl, B 4.0*M* HCl, C 5.9*M* HCl.

a) Absorption graph (5 min readings). *b*) Stability (absorbancy increase 5-30 min).

ment was obtained as shown in Fig. 4. The absorption peak in curve C of Fig. 2(a) was completely removed by the stannous chloride [compare with curve C Fig. 4(a)] thereby decreasing the possible blank contribution in the measurement of the absorbancy of a niobium solution. Of greater importance, however, is the improved stability of the solutions over a period of 30 minutes. According to this, therefore, the stannous chloride is a stabilizing reagent in addition to preventing any interference from ferric thiocyanate. A comparison of Fig. 3(a) with Fig. 4(a) also shows that the absorption is not due solely to stannous chloride, the amount contributed by the potassium thiocyanate increasing with the acidity.

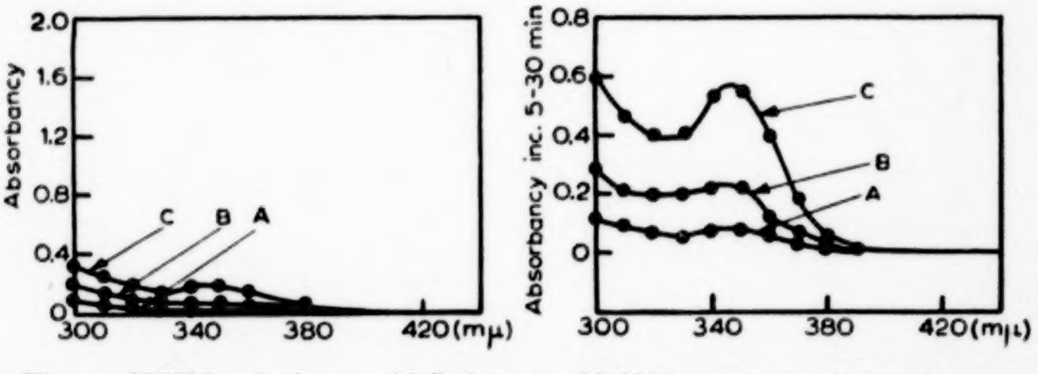

Fig. 5. KCNS solutions acidified to 2.3*M* HCl; acetone nil, $SnCl_2$ nil. A 0.48*M* KCNS, B 0.72*M* KCNS, C 0.96*M* KCNS.

a) Absorption graph (5 min readings). *b*) Stability (absorbancy increase 5-30 min).

The influence of stannous chloride was next investigated in potassium thiocyanate-hydrochloric acid solutions containing acetone. This study arose from FREUND AND LEVITT's observations on the enhancement of the colour from niobium thiocyanate by the addition of acetone. At the same time information was sought concerning the effects of varying the potassium thiocyanate concentration whilst maintaining the hydrochloric acid concentration fixed at 2.3*M*. The absorption spectra for potassium thiocyanate concentrations of 0.48, 0.72 and 0.96*M*, in the absence

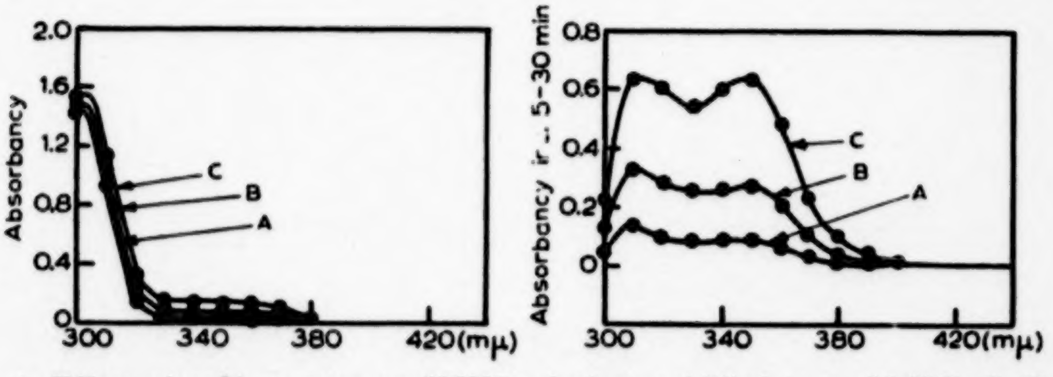

Fig. 6. Effect of 20% acetone on KCNS solutions acidified to 2.3*M* HCl; $SnCl_2$ nil. A 0.48*M* KCNS, B 0.72*M* KCNS, C 0.96*M* KCNS.

a) Absorption graph (5 min readings). *b*) Stability (absorbancy increase 5-30 min).

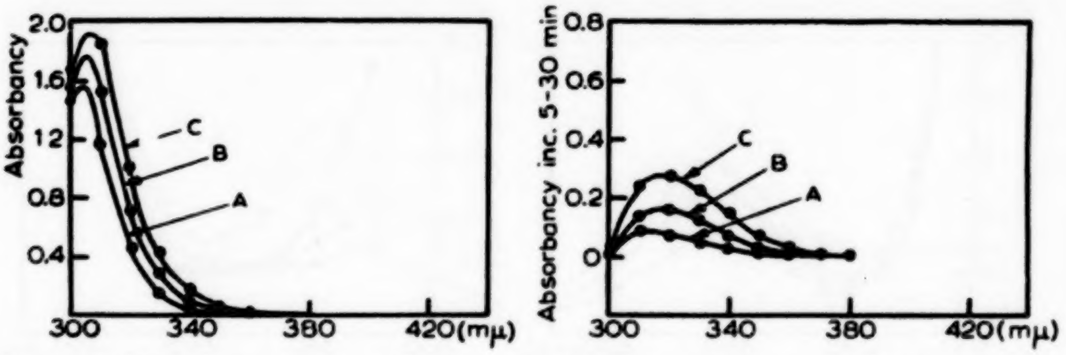

Fig. 7. KCNS solutions acidified to 2.3*M* HCl; acetone nil, $SnCl_2$ 0.02*M*.
A 0.48*M* KCNS, B 0.72*M* KCNS, C 0.96*M* KCNS.
a) Absorption graph (5 min readings). *b*) Stability (absorbancy increase 5-30 min).

of stannous chloride are shown in Fig. 5 and 6, the former referring to the absence of acetone and the latter to 20% v/v of this reagent. It is apparent that increasing the potassium thiocyanate concentration produces a similar but smaller effect to that obtained when the acidity is increased (*cf.* Fig. 5 and 2). The instability of the solutions in the absence of stannous chloride is clearly dependent, therefore, both on the acidity and the thiocyanate concentration. The addition of acetone resulted in no improvement of the stability but the absorbancy increased appreciably

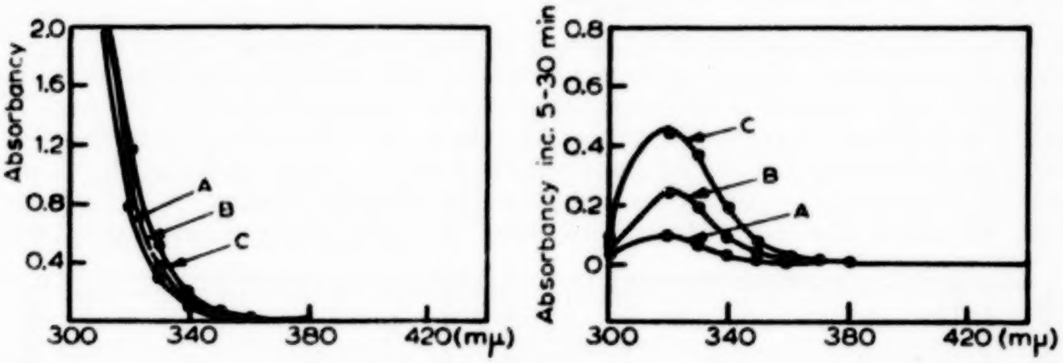

Fig. 8. Effect of 20% acetone on KCNS solutions acidified to 2.3*M* HCl; $SnCl_2$ 0.02*M*.
A 0.48*M* KCNS, B 0.72*M* KCNS, C 0.96*M* KCNS.
a) Absorption graph (5 min readings). *b*) Stability (absorbancy increase 5-30 min).

at wavelengths below 320 mμ in the presence of this reagent, an absorption maximum being indicated at 300 mμ (*cf.* Fig. 5 and 6). On repeating these experiments in the presence of 0.02*M* stannous chloride (Fig. 7 and 8), an appreciable improvement in stability was obtained both in the absence and presence of acetone, the stannous chloride again acting as a stabilizer [compare Fig. 5(b) with 7(b) and 6(b) with 8(b)]. It is clear from Fig. 7 that both greater absorbancy and instability result from increasing the thiocyanate concentration. In the presence of 20% acetone (see Fig. 8), the absorbancy of the solutions at low wavelengths again increased appreciably

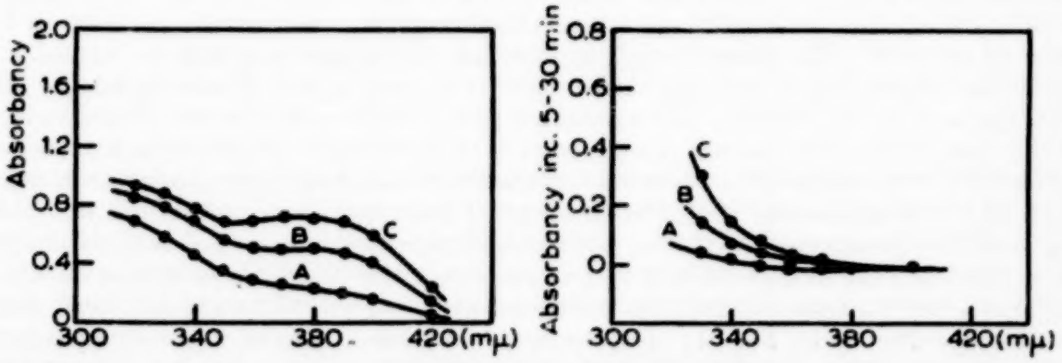

Fig. 9. Absorption by KCNS solutions when Nb is present; $SnCl_2$ 0.02*M*, acetone nil, HCl 2.3*M*, $C_4H_6O_6$ 0.032*M*, $KHSO_4$ 0.0085*M*, Nb 16 μg/ml;
A 0.48*M* KCNS, B 0.72*M* KCNS, C 0.96*M* KCNS.
a) Absorption graph (5 min readings). *b*) Stability (absorbancy increase 5-30 min).

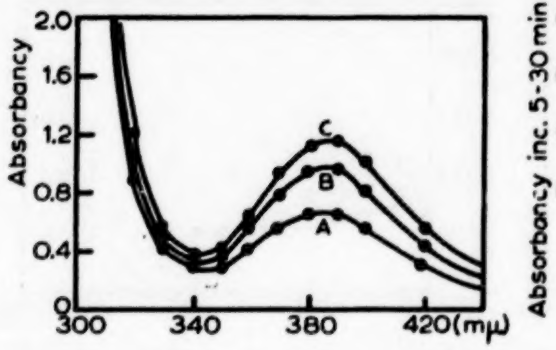

Fig. 10. Absorption by KCNS solutions when Nb is present. $SnCl_2$ 0.02*M*, acetone 20% v/v, HCl 2.3*M*, $C_4H_6O_6$ 0.01*M*, $KHSO_4$ 0.0015*M*, Nb 4 μg/ml;
A 0.48*M* KCNS, B 0.72*M* KCNS, C 0.96*M* KCNS.
a) Absorption graph (5 min readings). *b*) Stability (absorbancy increase 5-30 min).

and the instability of the solutions also increased. Even so the absorbancy of the acetone containing solutions is almost negligible for all the potassium thiocyanate concentrations studied at a wavelength of 385 mμ, which is the peak wavelength for the niobium thiocyanate complex.

(b) *Experiments in the presence of niobium*

To investigate niobium-containing solutions, a standard solution of this element was prepared by the accepted technique of fusing niobium pentoxide with potassium bisulphate and extracting the resultant melt with tartaric acid. Small amounts of potassium bisulphate and tartaric acid were, therefore, introduced with the niobium into the hydrochloric acid-potassium thiocyanate-stannous chloride solutions. According to FREUND AND LEVITT's findings, both sulphate and tartaric acid can decrease the absorbancy due to the niobium thiocyanate complex. In these investigations, therefore, the concentration of these two reagents was maintained at low levels.

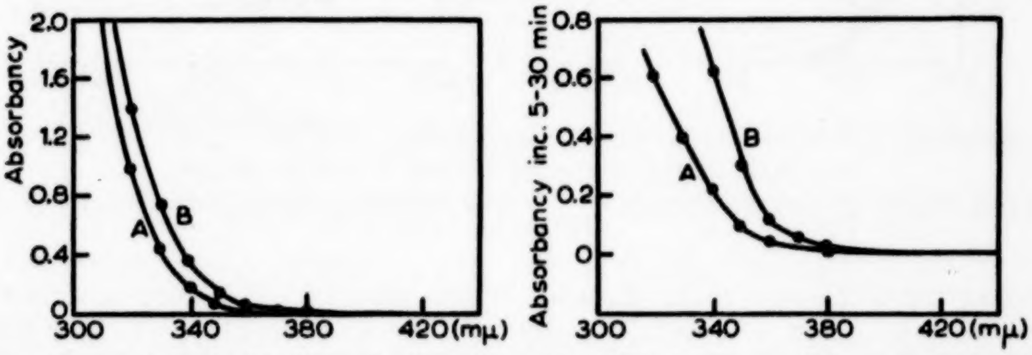

Fig. 11. Absorption by KCNS solutions at 3.6*M* HCl; $SnCl_2$ 0.02*M*, acetone 20% v/v,
A 0.48*M* KCNS, B 0.72*M* KCNS, salting at 0.80*M* KCNS.
a) Absorption graph (5 min readings). *b*) Stability (absorbancy increase 5-30 min).

In the first experiments the niobium thiocyanate complex was formed at a fixed acid concentration of 2.3*M* and at increasing potassium thiocyanate concentrations, both in the absence and presence of acetone. The absorbancy spectra for the niobium complex formed under these conditions are shown in Fig. 9 and 10, the former referring to the absence and the latter to the presence of acetone. The absorbancy of the niobium thiocyanate complex was found to increase with increase in the potassium thiocyanate concentration in both cases. In addition the absorbancy was greatly increased by the inclusion of acetone in the final solution; this can be seen by comparing Fig. 9 and 10 and is in agreement with the findings of FREUND AND LEVITT. This improvement in absorbancy must be connected with the niobium in solution, since the results of the previous section show conclusively that it could not occur from the reagents in solution. On extending the investigations to acetone-containing solutions at a higher hydrochloric acid concentration (3.6*M*), the results shown in Fig. 11 and 12 were obtained. Under these conditions it proved impossible to use a 0.96*M* concentration of potassium thiocyanate because of salting out difficulties; the maximum concentration studied being 0.72*M*. Again the absorbancy was found to be dependent on the potassium thiocyanate concentration, since it increased with larger concentrations of this reagent. A comparison of curve C of Fig. 12 with curve B of Fig. 10 shows that the absorbancy is also dependent on the acid concentration. Further comparisons showed that

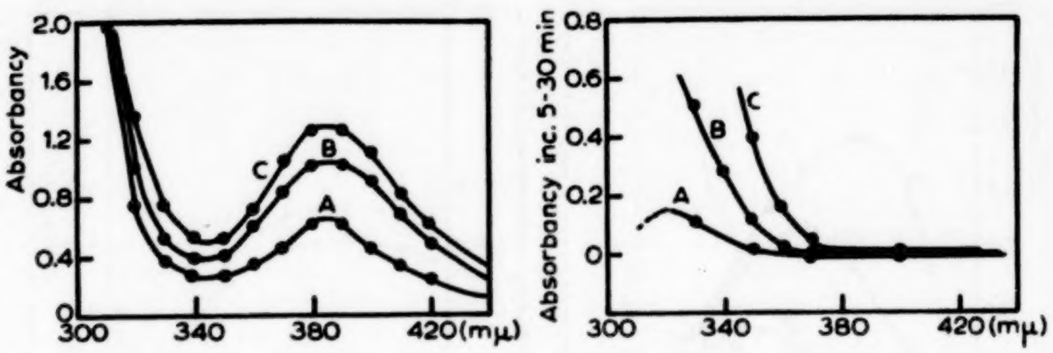

Fig. 12. Absorption by KCNS solutions, 3.6M in HCl when Nb is present; $SnCl_2$ 0.02M, acetone 20% v/v, Nb 4 μg/ml, $C_4H_6O_6$ 0.01M, $KHSO_4$ 0.0015M, A 0.24M KCNS, B 0.48M KCNS, C 0.72M KCNS.
a) Absorption graph (5 min readings). *b*) Stability (absorbancy increase 5-30 min).

in all cases, the absorbancy and instability of the niobium complex increased when either the acidity or the thiocyanate concentration was increased. Experiments were conducted, therefore, to determine whether there was a limiting acidity (or thiocyanate concentration) at which no further increase in absorbancy occurred.

2.2 *Experiments to determine optimum conditions*

Several series of experiments were carried out, each series at a fixed level of thiocyanate concentration but varying in acidity. A plot of the results obtained is shown in Fig. 13. With each series it can be seen that there is an optimum acidity at which maximum absorbancy is obtained, the value of this acidity moving to lower values as the thiocyanate concentration is increased. It is apparent, however, that even at 0.90M thiocyanate concentrations, maximum colour intensity has not been attained for the niobium. Furthermore the stability of the solutions at the optimum acidity is not satisfactory.

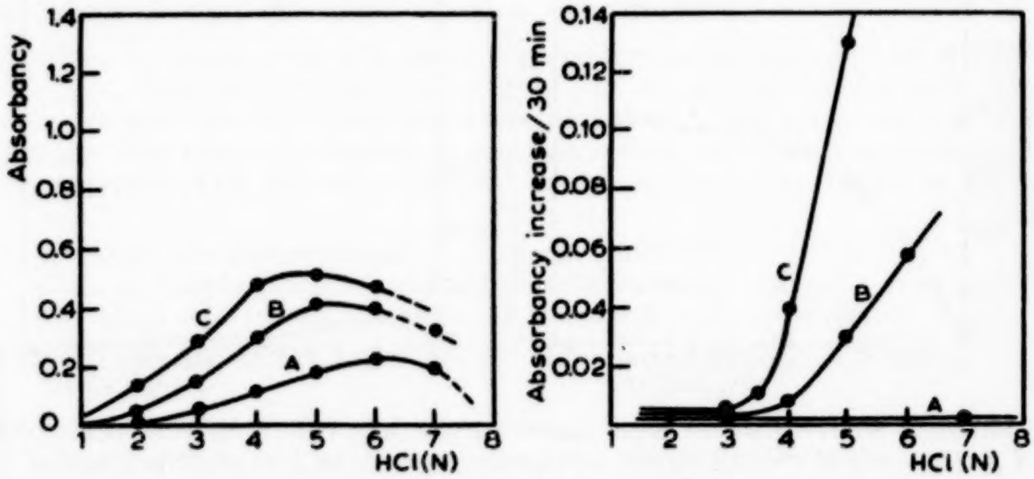

Fig. 13. Variation of acidity and thiocyanate without acetone; 385 mμ, 1 cm cells, temp. 22°. SO_4 0.007M, $C_4H_6O_6$ 0.10M, $SnCl_2$ 0.02M, Nb 4 μg/ml; A 0.30M KCNS, B 0.60M KCNS, C 0.90M KCNS.
a) Absorption graph (10 min readings). *b*) Stability (absorbancy increase /30min).

In subsequent experiments acetone was included to assist in the attainment of full colour development. Several further series of experiments were, therefore, conducted at a constant thiocyanate concentration of 0.30M, this low value being chosen to avoid the precipitation of potassium chloride at high acidities. Each series was at a fixed level of acetone, but varying in acidity. A plot of the results is shown in Fig. 14. Again each series showed an optimum acidity at which maximum absorbancy is obtained, the value decreasing with increase in the acetone concentration. Unlike the previous series, however, the stability of the solutions was only slightly affected by the increase in the acetone concentration.

It was considered that at high acetone concentrations the absorbancy of the niobium thiocyanate complex would be least affected by changes in the thiocyanate concentration and experiments were carried out in order to substantiate this view. The acetone concentration was increased

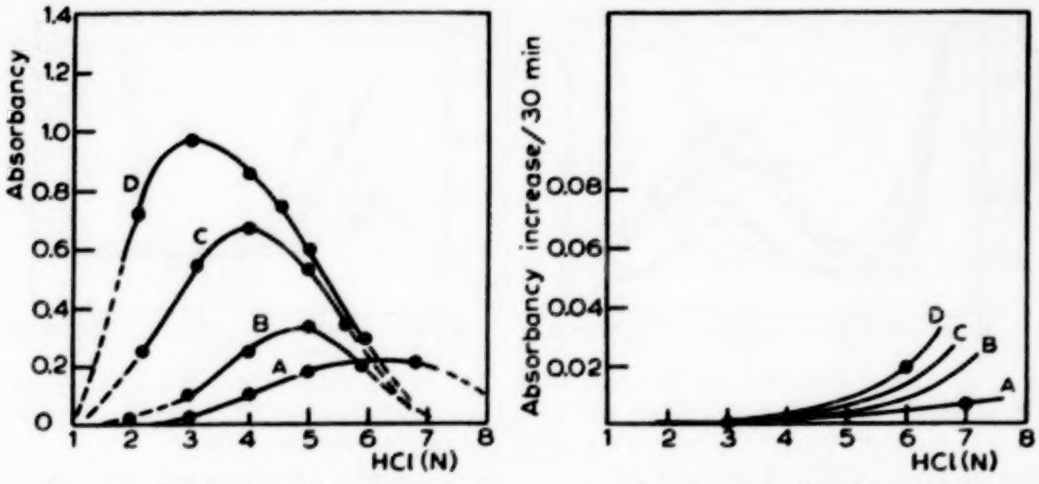

Fig. 14. Variation of acidity and acetone (thiocyanate level constant); conditions as in Fig. 13, KCNS 0.30M, Nb 4 μg/ml;
A no acetone, B 10% v/v acetone, C 20% v/v acetone, D 30% v/v acetone,
a) Absorption graph. *b*) Stability. Absorbancy increase /30 min.

to 50% v/v and from the previous experiments an acidity of 2.3N hydrochloric acid was chosen as being the probable value for maximum colour formation. In order to study high thiocyanate concentrations, the ammonium salt was used to avoid the difficulties arising from the precipitation of potassium chloride. A plot of the results of this series of experiments, in which only the thiocyanate concentration was varied, is given in Fig. 15. As with potassium thiocyanate, the absorbancy was found to increase with increase in the ammonium thiocyanate concentration. At the higher concentrations the niobium complex was only slightly affected by changes in the ammonium thiocyanate concentration. In addition the solutions were stable. The results of subsequent experiments to find the optimum concentration of hydrochloric acid under these conditions are shown in Fig. 16. It will be seen that both the optimum acidity (2M) and the absorbancy are only slightly affected by increasing the ammonium thiocyanate concentration from 0.3M to 0.6M. Further, at the optimum acidity the solutions were stable, particularly so at the higher thiocyanate concentration of 0.6M.

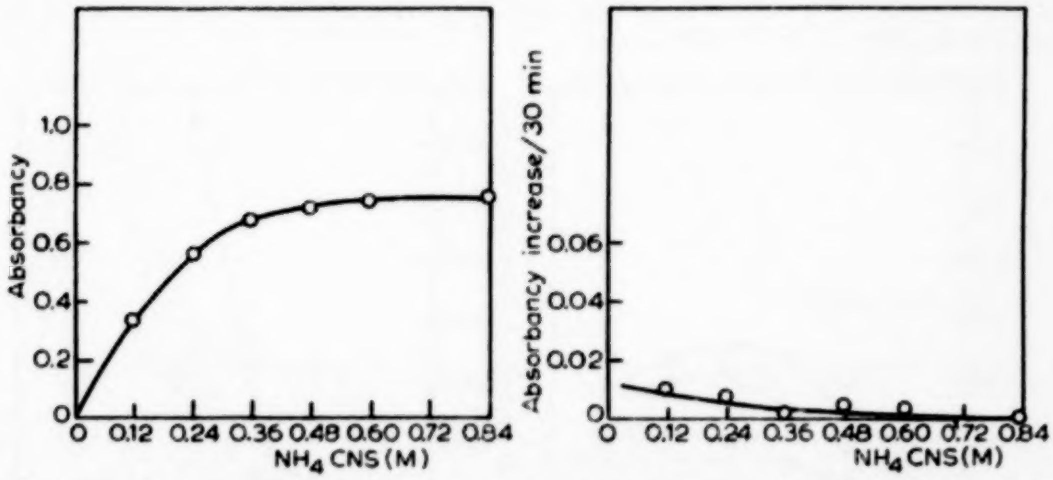

Fig. 15. Variation of thiocyanate at high acetone level, 385 mμ, S W 0.20 mm; SO_4 0.015M, $C_4H_6O_6$ 0.010M, $SnCl_2$ 0.02M, acetone 50% v/v, HCl 2.3N, Nb 2 μg/ml.
a) Absorption graph (5 min readings). *b*) Stability (absorbancy increase /30 min).

With solutions containing 50% by volume of acetone, some difficulty was experienced from the evaporation of acetone from the solution in an open absorptiometer cell. Moreover, creeping of the solution over the edges of the cell proved troublesome. Reliable absorbancy readings on these solutions could only be obtained by transferring the solution from stoppered flasks to the absorption cell and then taking readings without delay. These difficulties were greatly minimized, however, on decreasing the acetone concentration to 40% by volume and the following optimum solution conditions were formulated for the formation of a stable niobium thiocyanate complex-acetone 40%, hydrochloric acid 2.3M, ammonium thiocyanate 1M and stannous

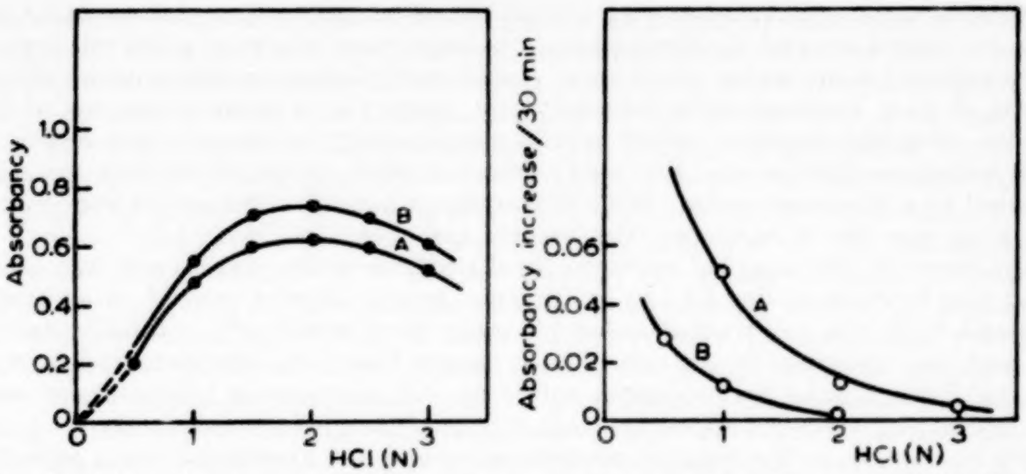

Fig. 16. Determination of optimum acidity; 385 mμ, S W 0.20 mm, SO_4 0.015*M*, $C_4H_6O_6$ 0.010*M*, $SnCl_2$ 0.020*M*, acetone 50% v/v, Nb 2 μg/ml;
A 0.30*M* NH_4CNS, B 0.60*M* NH_4CNS.
a) Absorption graph (5 min readings). *b*) Stability (absorbancy increase /30 min).

chloride 0.02*M*. The high concentration of ammonium thiocyanate was chosen because at this value small errors in the preparation of this solution should only slightly affect the absorbancy of the niobium thiocyanate complex. With several separate supplies of ammonium thiocyanate taken from freshly opened bottles, the absorbancy of the thiocyanate complex for 100 μg of niobium varied by less than ± 0.005 from the standard value of 0.79. With the wet material from previously opened bottles, however, ammonium thiocyanate solutions 10 to 20% low in molarity were obtained and solutions from such material could not be used without volumetric standardization and adjustment. Also at this high thiocyanate concentration, there is very little loss in sensitivity with a decrease in the acetone concentration.

2.3 Experiments to test the final solution conditions

In experiments to test these conditions, a composite solution was used for the acetone and the hydrochloric acid. This was prepared by adding 147 ml of hydrochloric acid (sp.gr. 1.18) to 58.8 ml of water in a 500 ml volumetric flask and then diluting the solution to volume with AnalaR acetone. This solution develops a greenish colour very slowly and, therefore, should be prepared as required. The following solution additions were then made to 50 ml volumetric flasks:

34 ml of the hydrochloric acid-acetone mixture.
5 ml of 0.05*M* tartaric acid solution containing niobium.
0.5 ml of 2*M* stannous chloride in concentrated hydrochloric acid.
9 ml of 6*M* ammonium thiocyanate (228 g of solid/500 ml).

After dilution to volume with water, the solution was allowed to attain a uniform temperature (23° C) by immersion in a thermostat bath for 5 to 10 minutes. Then absorbancy measurements

TABLE I

RESULTS FOR THE ABSORBANCY OF THE NIOBIUM THIOCYANATE COMPLEX WITH INCREASE IN NIOBIUM CONCENTRATION

Niobium (μg/ml)	*Absorbancy*	*Absorbancy corrected for blank*	*Deviation from mean*
0	0.011	0.000	
0.4	0.170	0.159	nil
0.8	0.330	0.319	<0.001
1.2	0.491	0.480	+0.002
1.6	0.649	0.638	+0.001
2.0	0.803	0.792	—0.004

Mean = 0.398/μg/mlNb Std. devn. = ±0.002A were taken using a spectrophotometer with a modified cell chamber to enable constant temperature water to be circulated around it. Absorbancy readings were taken at a wavelength of 385 mμ using a 1 cm cell and a slit width of 0.2 mm. A standard niobium solution was prepared by dissolving 20 mg of pure niobium metal in nitric acid, using the minimum amount of hydrofluoric acid to obtain complete solution. After careful evaporation to dryness, the residue was fused with 1 g of potassium bisulphate, the melt extracted with 50 ml of *M* tartaric acid and the solution diluted to 1 litre with water. With this solution a calibration graph was prepared in the range 0 to 2 μg per ml of niobium; the results are given in Table I.

Control solutions at the 2 μg/ml niobium level confirmed the stability of the stock niobium solution and the reproducibility of the calibration graph. Over a period of several weeks, no control differed from the calibration value by more than about 1%. Stability tests were also conducted and no increase in absorbancy by more than 0.01 was detected over a period of 30 minutes for both blanks and niobium solutions. An increase in temperature was found to result in increased absorbancies approximately 1% for a change in temperature from 18° to 23° C.

The effects of changes in the reagent concentrations on the absorbancy of 2 μg/ml of niobium was also investigated. The reagents were varied individually by ± 10% from the proposed concentrations with the following errors in the niobium determinations:

Reagent (change in concentration)	+ 10%	— 10%
Acetone	*	< 1%
Hydrochloric acid	*	< 1%
Ammonium thiocyanate	< 1.5%	< 1.5%

* Impossible to obtain absorbancy measurements because of salting out effects.

These results show conclusively that the degree of complexation of the niobium with thiocyanate is only slightly changed by major changes in the reagent concentrations.

Experiments were also carried out to study the effects of the potassium bisulphate and tartaric acid concentrations on the absorbancy since both these reagents are used in the preparation of the niobium solution and FREUND AND LEVITT found that both influenced the absorbancy of the niobium thiocyanate complex prepared according to their conditions. Under the solution conditions recommended in this paper, however, potassium bisulphate concentrations up to 0.18*M* and tartaric acid concentrations up to 0.20*M* did not affect the slope of the calibration graph. The absorbancy of the reagent blank increased slightly with increase in tartaric acid concentration, but the absorbancy difference for solutions containing niobium was unaffected. This behaviour is of major importance in the use of the niobium thiocyanate complex in applied analysis, since it avoids the need for strict control of the reagents used in the preparation of niobium solutions.

2.4 *Interference from other elements*

The absorbancies due to other elements under the optimum conditions for the niobium thiocyanate complex is of importance in a consideration of the analytical applications of this complex. Several elements including molybdenum, tungsten, uranium, titanium and iron are capable of giving coloured thiocyanate complexes and are, therefore, potential interfering elements in the determination of niobium. Experiments were, therefore, carried out to test the behaviour of other elements under the proposed solution conditions. The results of these experiments are given in Table II.

TABLE II

THE PERCENTAGE ERROR IN THE DETERMINATION OF 2 μg/ml OF NIOBIUM CAUSED BY INTERFERING ELEMENTS

Interfering element	*Error when the ratio of interfering element to niobium is* *10 to 1* %	*1 to 1* %
Molybdenum	70	3.7
Tungsten	14	5.0
Tantalum	3.3	1.0
Iron	2.5	nil
Titanium	—	120
Vanadium	—	30
Uranium	12	1.2
Chromium	< 1.0	nil

Some of the results in Table II can only be regarded as giving an indication of the order of the error to be expected since the thiocyanate complexes were not stable. In the case of molybdenum, for example, the absorbancy decreased fairly rapidly with time, whereas with tungsten, tantalum, vanadium and chromium there was a slight increase in the absorbancy with time.

The major difference between these conditions and those recommended by FREUND AND LEVITT is the behaviour of titanium. These latter workers found no interference for the 1 to 1 ratios of TiO_2 to Nb_2O_5 and this behaviour proved of value in the determination of the niobium content of Sukulu ores and granites[4]. The improved stability of the niobium thiocyanate complex under the new conditions is, therefore, offset by the greatly increased interference from titanium. This latter element is often found associated with niobium and in the application of the thiocyanate complex some separation of these elements may be necessary. Fortunately the partition coefficient for titanium in the solvent extraction of niobium into hexone from hydrofluoric and sulphuric acid solutions is low and the separation of these elements is readily attainable[5]. In cases where the niobium to titanium ratio is high, however, it is possible to apply a correction for titanium, since this element gives a linear calibration over the range 0 to 1.0 μg per ml of titanium under the conditions for the formation of the niobium thiocyanate complex. The size of the correction is dependent to some extent on the concentration of niobium present and it is not highly reproducible. The correction to be applied is of the order of 1.2% Nb for every 1% Ti and titanium corrections can only be applied, therefore, when the titanium concentration is low, if serious errors are to be avoided.

THE DETERMINATION OF NIOBIUM IN STAINLESS STEEL

Stainless steels which have been stabilized with niobium generally contain amounts of this element varying up to about 1.5%. The titanium content is very much smaller and the ratio of Nb to Ti is favourable for the thiocyanate procedure. In contrast the high iron to niobium ratio would result in appreciable errors from the iron without some preliminary separation. Cupferron is used to separate the niobium from many alloying constituents in a gravimetric method for this determination[6], the majority of the iron being retained in the solution in the reduced state. In studying the possible application of the thiocyanate method to this determination, therefore, this separation procedure was employed. It is not suggested that this is the best method for the separation of niobium from other steel constituents, but it was convenient in this instance since titanium is also precipitated by the cupferron and its contribution to the absorbancy could be allowed for. The steel sample is dissolved as much as possible in sulphuric acid and the addition of an oxidizing agent to break down carbides is avoided. This is essential to keep the iron in the reduced condition. A critical examination of the solution procedure showed that the majority of the niobium does not go into solution and the cupferron precipitation, therefore, ensures the recovery of the small amount which might pass into solution. Details of the method employed in this investigation are as follows:

Dissolve 1 g of sample in 75 ml of diluted sulphuric acid (1+4). Cool, dilute to a volume of 100 ml with water and thoroughly cool in running water. Mix a small amount of paper pulp with the solution and then add 5 ml of 6% cupferron solution dropwise with constant stirring. Allow to stand in the cold for 30 minutes, then filter through a Whatman No. 41 filter paper, containing a little paper pulp, washing the precipitate with cold 5% v/v sulphuric acid containing 1 ml of the cupferron reagent solution per litre. Then finally wash five times with cold diluted ammonium hydroxide (5+95) to remove tungsten, molybdenum etc. Transfer the filter paper and precipitate to a platinum dish, dry and finally ignite at a temperature of 650° C. Cool, add 2 ml of diluted sulphuric acid (1 + 4) and 5 ml of hydrofluoric acid (40%) and evaporate to dryness to remove silica. Fuse the residue with 1 g of potassium bisulphate at a low temperature and extract the cooled melt in 50 ml of 0.5*M* tartaric acid. Dilute this solution to 500 ml with water. Take a 5 ml aliquot for the formation of the niobium thiocyanate colour and take absorbancy readings as previously described. Correct the reading for the titanium content of the sample and obtain the niobium concentration by referring the corrected reading to the niobium calibration graph.

Typical results obtained on applying this procedure to samples of stainless steels are given in Table III, the sum of the niobium and tantalum figures agreeing reasonably well with the gravimetric results for these elements.

TABLE III

RESULTS FOR NIOBIUM IN STAINLESS STEELS BY THE THIOCYANATE PROCEDURE

Sample No.	*Titanium* %	*Niobium by thiocyanate*** %	*Tantalum by activation** %	*Gravimetric result for niobium (+ tantalum)* %
B.C.S. 246	nil	0.79	0.035	0.82
1	0.18	1.04	0.10	1.17
2	0.10	0.62	0.055	0.69
3	0.05	1.04	0.09	1.16

* Results reported by Mr. A. A. SMALES.
** Average figures for many determinations.

SUMMARY

Solution conditions for the formation of the niobium thiocyanate complex in an aqueous-acetone homogeneous medium have been examined in detail. New conditions have been developed for the formation of a stable thiocyanate complex, such that its absorbancy is not critically dependent upon changes in the reagent concentrations. Linear and reproducible calibration graphs are produced for amounts of niobium in the range 0 to 2 μg/ml and a wide range in the amounts of potassium bisulphate and tartaric acid used in the preparation of the niobium solutions is permissible. Titanium gives rise to interference, but for low ratios of titanium to niobium it is possible to apply a correction for this element. For high ratios the separation of the niobium from the titanium is desirable.

RÉSUMÉ

Les conditions de formation du complexe niobium-thiocyanate en milieu eau-acétone ont été étudiées. De nouvelles conditions sont données pour la formation d'un complexe stable, dont l'absorption ne varie pas sensiblement avec des changements de concentration du réactif. Les courbes d'étalonnage, obtenues avec des teneurs en niobium allant de 0 à 2 μg/ml, sont linéaires et reproductibles; des quantités très variables de bisulfate et d'acide tartrique (provenant de la préparation des solutions de niobium) peuvent être présentes. Le titane gêne, mais pour de faibles rapports titane/niobium, il est possible d'utiliser un facteur de correction. Pour des rapports plus grands, la séparation niobium-titane est recommandée.

ZUSAMMENFASSUNG

Die Bedingungen unter welchen sich die Niob-Thiocyanat-Komplexverbindung in einem homogenen wässrig-acetonischen Medium bildet, wurden eingehend untersucht. Es wurden neue Bedingungen für die Bildung eines Komplexes ermittelt, dessen Absorption bei Änderungen der Reagenzkonzentration nicht wesentlich variiert. Die Eichkurven sind für Niobmengen bis zu 2 μg/ml lineär und reproduzierbar; stark wechselnde Mengen an Kaliumbisulphat oder Weinsteinsäure (welche von der Herstellung der Nioblösungen herrühren) stören nicht. Titan stört, aber wenn das Verhältnis Titan:Niob klein ist, kann man einen Korrekturfaktor anwenden; ist dieses Verhältnis grösser, so ist es ratsam, das Niob vom Titan zu scheiden.

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THE SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM AS THIOCYANATE IN ACETONE-WATER MEDIUM*

by

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INTRODUCTION

While studying the method for the spectrophotometric determination of uranium by thiocyanate in acetone-water medium[1], it was observed that under approximately similar conditions vanadium gave a blue color. The absorption of the vanadium thiocyanate blue in acetone-water is greater than that of the blue vanadyl ion[2], and experiments were performed to test its applicability to the determination of vanadium.

Absorption spectra of V(III and IV) thiocyanate in aqueous solution were reported by FURMAN AND GARNER[3], and CROUTHAMEL, JOHNSON, AND HJELTE[4] reported absorption spectra of V(III) thiocyanate in acetone-water solution.

This work was done as part of a program conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

EXPERIMENTAL DATA

Reducing agent. Stannous chloride could not be used because, under even the most favorable conditions, it caused the solution to turn cloudy. Hydroxylamine hydrochloride, although satisfactory in this respect was sluggish in its action, but it finally gave the maximum absorbancy under the experimental conditions for the quantities of vanadium determined. Sulfurous acid reacted rapidly and appeared to increase the stability of the final color.

Thiocyanate and sulfuric acid concentrations. It was observed early that for certain combinations of thiocyanate and sulfuric acid concentrations in a 3:2 acetone-water mixture, separation of two phases occurred, with or without the simultaneous separation of a white solid. Accordingly, a study was made of the range of useful concentrations of ammonium thiocyanate sulfuric acid in 3:2 acetone-water medium. In the region below the curve in Fig. 1, the various combinations of ammonium thiocyanate and sulfuric acid gave a homogeneous solution. For studying the absorbancy of the system, a solution 1 molar in ammonium thiocyanate and 0.14 normal in sulfuric acid was used.

Acetone. Both acetone and thiocyanate have to be used in order to obtain an increased sensitivity. Acetone has been used previously for such a purpose in the determination of uranium[1], cobalt[5], and iron[7]. In the absence of thiocyanate, acetone does not increase the absorbancy of the blue vanadyl ion formed by sulfurous acid reduction[2].

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* Publication authorized by the Director, U. S. Geological Survey.

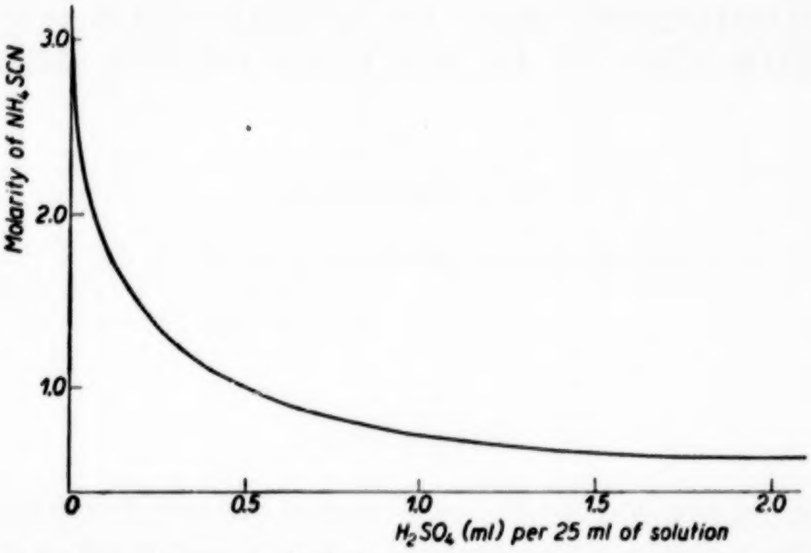

Fig. 1. Area of usefulness of NH_4SCN-H_2SO_4 in 3:2 acetone-water mixture.

Absorption spectrum of V(IV) thiocyanate. The absorbancy of the blue compound produced by vanadium, sulfurous acid, and thiocyanate in 3:2 acetone-water was measured with a quartz photoelectric spectrophotometer using 1-cm cells. The absorption spectrum, Fig. 2, shows a maximum absorbancy at 750 mμ.

Conformance to Beers law at 750 mμ is shown in Fig. 3. The sensitivity of this system is not as great as that of the peroxide system[6], but is 4 to 5 times as great as the vanadyl blue system[2].

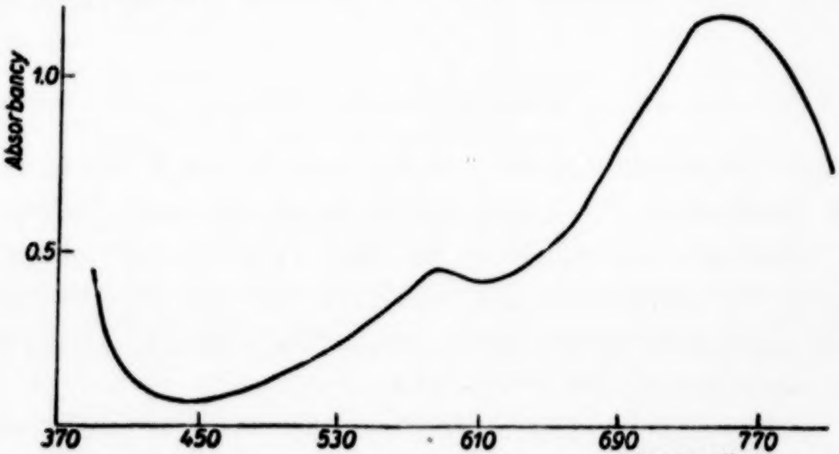

Fig. 2. Spectrum of vanadium(IV) thiocyanate.

Interfering elements. No attempt was made to study this reaction in the presence of other elements; however, vanadium is often separated from many interfering elements as the cupferride[8] and converted to a sulfuric acid solution. Macro quantities of vanadium are then determined volumetrically. The method here developed is suggested in place of the volumetric procedure.

It should be emphasized that before this procedure is applied to other than pure vanadium solutions, the effect of other elements present should first be determined, and if they are found to interfere, the necessary separations should be made.

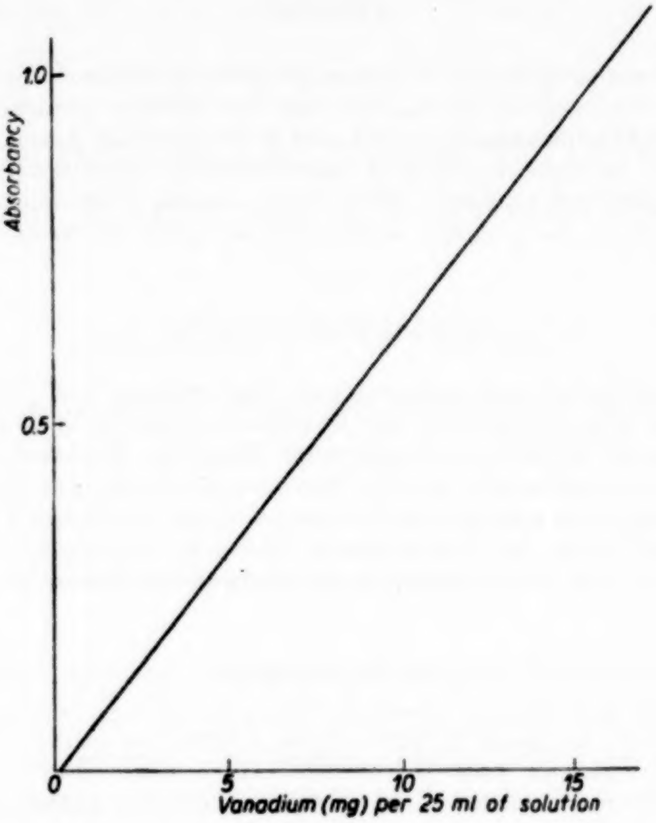

Fig. 3. Working curve.

PROCEDURE

Apparatus

Quartz photoelectric spectrophotometer.
1-cm corex cells.

Reagents and solutions

Sulfurous acid, not less than 6%, analysed reagent.
Acetone, reagent grade or redistilled.
Ammonium thiocyanate, $8.33M$.

Dissolve 158.5 g of ammonium thiocyanate, A.C.S. grade, in distilled water with slight warming, cool, dilute to 250 ml in a volumetric flask and filter through a dry filter.

Standard vanadium solutions were prepared from a stock solution of potassium vanadate (1 ml = 0.033 g V_2O_5) that had been analysed volumetrically.

Detailed procedure

A 5-ml aliquot of the prepared vanadium solution free of interferences, containing between 5 and 15 mg of vanadium and 0.1 ml of free sulfuric acid, is transferred to a 25-ml volumetric flask. The reagents are pipetted into the flask in the following order, mixing after each addition: 1 ml of sulfurous acid solution, 15 ml of acetone, 3 ml of $8.33M$ ammonium thiocyanate, and finally water to the mark.

The absorbancy is measured against distilled water, as a reference solution, with a quartz photoelectric spectrophotometer using 1-cm cells at a wavelength of 750 mμ. The concentration of vanadium can be read from a curve prepared in the same manner from standard vanadium solutions (Fig. 3). The color developed under these conditions is stable for at least 48 hours.

SUMMARY

A method devised for the spectrophotometric determination of vanadium in acetone-water medium is based on the reaction between vanadium(IV) and thiocyanate. Within the concentration limits tested, Beers law is obeyed.

This method is not as sensitive as the peroxide method, but the vanadium(IV)-thiocyanate reaction product shows greater absorbancy than the blue vanadyl ion. In the absence of interfering elements, the method can be used in place of the volumetric procedure for the determination of macro quantities of vanadium.

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RÉSUMÉ

Une nouvelle méthode est proposée pour le dosage spectrophotométrique du vanadium dans un milieu eau-acétone; elle est basée sur la réaction obtenue entre le vanadium(IV) et le thiocyanate. Dans les limites de concentrations essayées, la loi de Beer est obéie. La méthode est moins sensible que celle au peroxyde; le produit de réaction vanadium(IV)-thiocyanate présente cependant une absorption plus grande que l'ion vanadyle bleu. En l'absence d'éléments gênants, cette méthode peut être utilisée à la place du procédé volumétrique, pour le dosage de macroquantités de vanadium.

ZUSAMMENFASSUNG

Eine neue Methode zur spektrophotometrischen Bestimmung von Vanadin in Wasser-Aceton wurde vorgeschlagen; sie gründet sich auf die Reaktion zwischen Vanadin(IV) und Thiocyanat. Innerhalb der untersuchten Konzentrationsgrenzen, folgt die Reaktion dem Beer'schen Gesetze. Diese Methode ist nicht so empfindlich wie die Peroxyd-Methode; das Produkt der Vanadin (IV)-Thiocyanat-Reaktion zeigt aber eine grössere Absorption als das blaue Vanadylion. Bei Abwesenheit störender Elemente kann die beschriebene Methode an Stelle des volumetrischen Verfahrens zur Bestimmung von Makro-Mengen an Vanadin angewendet werden.

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DOSAGE SPECTROPHOTOMÉTRIQUE DE PETITES QUANTITÉS DE VANADIUM À L'AIDE DE LA DIPHÉNYLBENZIDINE

par

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INTRODUCTION

La diphénylbenzidine, connue et employée depuis longtemps pour la détection des nitrates, a été décrite par J. HOSTE[1] comme réactif spécifique et très sensible pour la détection du vanadium sous forme d'ions VO_3^-: on obtient un précipité vert foncé avec les solutions à concentration élevée en vanadium, tandis que les solutions diluées donnent lieu à une coloration jaune, perceptible jusqu'à 0.25 γ de vanadium, la limite de dilution étant $D = 10^{-6}$ sur plaque à godets. D'après l'auteur il n'y aurait que les ions oxydants qui gênent la réaction. Comme les bonnes méthodes analytiques pour le dosage de petites quantités de vanadium sont toujours peu nombreuses, nous avons étudié cette réaction pour voir sous quelles conditions elle se prêterait au dosage spectrophotométrique de cet élément.

ESSAIS PRÉLIMINAIRES

Solution standard

Une solution contenant 1 mg de vanadium/ml a été préparée par dissolution dans l'eau bidistillée de la quantité calculée de métavanadate d'ammonium, produit Kahlbaum puriss.

La teneur exacte en vanadium de la solution a été contrôlée par dosage potentiométrique.

Les solutions nécessaires aux différents essais sont obtenues à partir de cette solution standard par dilution adéquate.

Solution du réactif.

Comme réactif nous avons employé la diphénylbenzidine pure d'origine Eastman Kodak ou British Drug Houses (B.D.H.). La quantité désirée est mise en solution par chauffage en vase de Berlin. Après dissolution complète, on laisse refroidir, on transvase dans un ballon jaugé et on remplit jusqu'au trait.

Pour la détection du V^{+5}, HOSTE[1] a employé une solution saturée du réactif dans l'acide acétique. Nous avons étudié plusieurs autres solvants: l'acétone, le toluène, le benzène, l'acétate d'amyle, l'alcool hexylique normal, l'alcool iso-amylique. Tous ces solvants étaient des produits p.a. ou fraîchement distillés. Des essais comparatifs avec une solution aqueuse de V^{+5} ont montré que la couleur ne se développe qu'en milieu acide, mais disparaît cependant rapidement quand le pH diminue au delà d'une certaine limite. Il s'avérait qu'une solution acétique du réactif est à préférer tant au point de vue sensibilité qu'au point de vue stabilité de la coloration obtenue.

Limites des concentrations utilisables

La diphénylbenzidine est très peu soluble dans l'eau. Lorsqu'on ajoute une solution aqueuse de vanadium à une solution acétique concentrée du réactif, celui-ci précipite, donnant lieu à une opalescence d'autant plus intense que la concentration du réactif dans la solution est plus grande et que le rapport du volume de la solution aqueuse au volume de la solution acétique est plus élevé. Ainsi, pour une solution du réactif à $8 \cdot 10^{-3}$ %, ce dernier rapport ne peut dépasser la valeur de 1:10.

D'autre part la réaction change d'aspect en fonction de la concentration en vanadium, passant d'une coloration jaune à un précipité vert. La formation du précipité vert ne dépend pas seulement de la concentration de V^{+5}, mais plutôt du rapport V/réactif. Il est possible que le complexe vert se forme entre la forme oxydée de la diphénylbenzidine et les ions V^{+5}. FEIGL[2] a prononcé d'ailleurs une même hypothèse pour expliquer la réaction entre V^{+5} et la 3-3′ diméthylnaphtidine, décrite par BELCHER, NUTTON ET STEPHEN[3].

Pour obtenir la coloration jaune il faut un excès de réactif. Comme il n'est pas souhaitable d'employer des solutions trop diluées de ce dernier, nous avons déterminé les limites des concentrations en vanadium donnant lieu à la coloration jaune dans les conditions opératoires suivantes: 1 ml de solution aqueuse de vanadium + 10 ml de solution acétique du réactif à $8 \cdot 10^{-3}$ %. Nous avons trouvé que la réaction est utilisable pour des concentrations en vanadium à partir de 10^{-4} % jusqu'à $4 \cdot 10^{-3}$ %. La coloration se développe lentement et atteint un maximum sensiblement constant après un temps variable d'après la concentration de la solution en vanadium.

Courbe d'extinction

La courbe d'extinction de la solution jaune obtenue en mélangeant 1 ml d'une solution à 10^{-3} % de vanadium, avec 10 ml d'une solution du réactif à $8 \cdot 10^{-3}$ %, est représentée dans la Fig. 1.

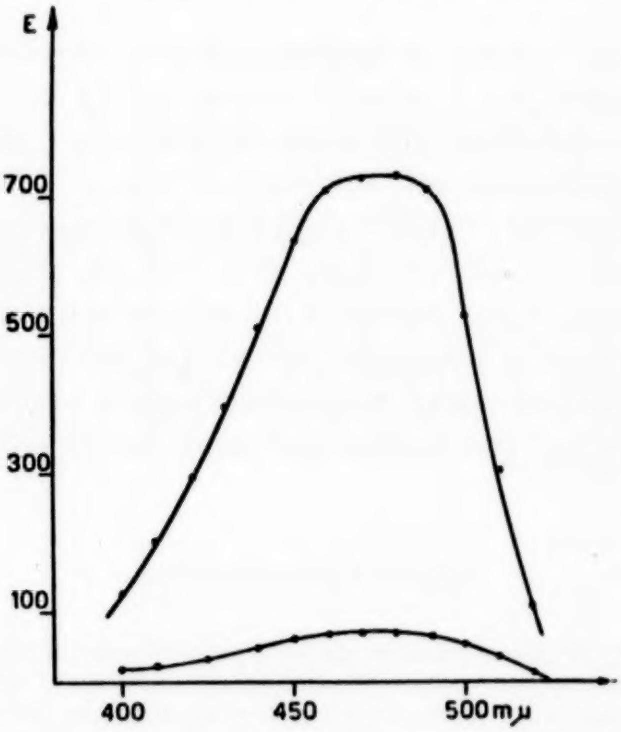

Fig. 1. Courbes d'extinction

Les mesures sont faites au spectrophotomètre Beckman DU, entre 400 et 520 mμ. Comme blanc nous employons le réactif dilué à l'eau dans le rapport 10 : 1.

Dans la même figure nous avons indiqué la courbe d'extinction de la solution du réactif, mesurée par rapport à l'eau distillée.

La bande d'absorption présente un maximum assez large entre 470 mμ et 485 mμ. Le maximum d'absorption pour la solution du réactif est trouvé également à 480 mμ.

Dans toutes les expériences suivantes l'extinction a été mesurée pour la longueur d'onde de 480 mμ, par rapport à la solution du réactif, diluée avec la même quantité d'eau que la solution mesurée.

INFLUENCE DE DIFFÉRENTS FACTEURS

Stabilité de la solution du réactif

La solution du réactif, pratiquement incolore au moment de la préparation, prend lentement une coloration jaune pâle. L'extinction de la solution, mesurée par rapport à l'eau distillée, augmente de 0.013 pour la solution fraîchement préparée jusqu'à 0.055 après 48 h. La vitesse de la coloration augmente sous l'influence de l'air et de la lumière. Pour une solution conservée en vase ouvert l'extinction atteint 0.084 après 3 h, tandis que nous mesurons 0.021 après 48 h pour une solution conservée dans un flacon brun bien fermé.

L'apparition de la coloration jaune dans la solution du réactif est accompagnée d'une augmentation de la réactivité du produit. L'extinction mesurée d'une même solution vanadique avec la même solution du réactif conservé à l'abri de la lumière, mesurée par rapport à la solution du réactif comme blanc, reste sensiblement constante pendant plusieurs jours. A partir du septième jour, l'extinction augmente progressivement, l'augmentation atteignant ± 10% après 15 jours.

L'augmentation de la température favorise l'altération de la solution du réactif. Ainsi la température et la durée de chauffe pour la dissolution du réactif ne sont pas sans influence. Employant des solutions du réactif préparées par chauffage pendant un même temps à la même température (bain-marie), la déviation moyenne sur l'extinction mesurée d'une même solution de vanadium restait inférieure à 1%. Elle était de l'ordre de 7% avec des solutions préparées par chauffage au bec jusqu'à dissolution.

L'origine (qualité) du réactif a également une influence non négligeable. Ainsi l'extinction mesurée pour une même solution de vanadium, avec une solution du réactif préparée à partir d'un produit Eastman Kodak, dépasse de 8% celle obtenue avec une solution du produit B.D.H.

Il s'en suit que toutes les solutions standards et les solutions inconnues seront mesurées avec la même solution du réactif.

Influence du rapport eau: HAc

La solution de l'essai à blanc, préparée par dilution de 10 ml de la solution acétique de la diphénylbenzidine avec 1 ml d'eau distillée, parfaitement claire au début, devient légèrement opalescente après quelques heures. La précipitation du réactif peut être évitée en diminuant la proportion de l'eau dans la solution finale.

Dans une série d'essais la solution aqueuse de vanadium à 10^{-3} % a été remplacée par une solution de vanadium, d'une part dans l'acide acétique pur, d'autre part, dans des mélanges d'acide acétique et d'eau à rapport 9 : 1, 3 : 1 et 1:1.

Aucune opalescence n'a été constatée avec ces solutions, même après plusieurs jours, et en employant une solution plus concentrée du réactif à 10^{-2}%.

Lorsque le rapport acide acétique: eau dans la solution vanadique surpasse la valeur de 3 : 1, la coloration se développe instantanément, mais l'intensité diminue rapidement.

Pour les rapports acide acétique: eau de 3:1 et de 1:1, l'intensité de la couleur atteint un maximum après 3 à 10 min et reste constante pendant plus de 30 min. La reproductibilité des mesures obtenue avec ces solutions est également satisfaisante.

Dans les expériences suivantes on a employé une solution de V^{+5} dans un mélange acide acétique: eau = 1:1.

Stabilité de la solution acétique du vanadium

L'extinction mesurée pour une même solution de V^{+5} dans un mélange acide acétique: eau = 1:1, et une solution fraîche du réactif, diminue en fonction du temps.

Les deux premières colonnes du Tableau I donnent l'extinction pour une solution

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à 4·10⁻⁴% de vanadium, mesurée immédiatement après la préparation et après un délai de 8 jours. Dans la troisième colonne figure le résultat obtenu avec cette dernière solution après oxydation par quelques gouttes de $KMnO_4$ 0.005*N*, dont l'excès a été détruit par chauffage à 70° jusqu'à décoloration complète. Le réactif employé est un produit B.D.H.

TABLEAU I

EXTINCTION D'UNE SOLUTION DE V^{+5} À $4 \cdot 10^{-4}\%$ DANS LE MÉLANGE HAc:EAU = 1:1

No.	*Immédiatement après préparation*	*Après 8 jours*	*Après oxydation au $KMnO_4$*
1	0.225	0.200	0.226
2	0.223	0.199	0.227

La diminution de l'extinction est probablement due à la réduction des ions V^{+5} par des traces d'impuretés réductrices (HCOOH, CH_3-CO-CH_3) dans l'acide acétique employé. Ainsi il est recommandable d'oxyder au préalable par le $KMnO_4$ les substances réductrices de l'acide acétique employé et d'ajouter l'acide à la solution aqueuse de vanadium immédiatement avant l'emploi.

Influence du pH

Les conditions expérimentales déterminées dans les essais précédents ne permettent guère de grandes variations du pH de la solution finale. On a pu montrer cependant que l'augmentation de l'acidité — en employant une solution de vanadium dans l'acide acétique pur ou en introduisant des acides forts — donne lieu à une coloration plus intense mais de stabilité d'autant plus faible que le pH diminue. D'autre part, l'augmentation du pH réduit l'intensité de la coloration.

Excès du réactif

L'influence de la quantité de diphénylbenzidine sur la coloration obtenue a été étudiée pour différentes concentrations de vanadium, variant de 10^{-4} à $10^{-3}\%$. Le rapport entre le volume de la solution de vanadium, et le volume de la solution du réactif est tenu constant à 1:10, mais la concentration du réactif dans la solution varie de $10^{-3}\%$ à $10^{-2}\%$.

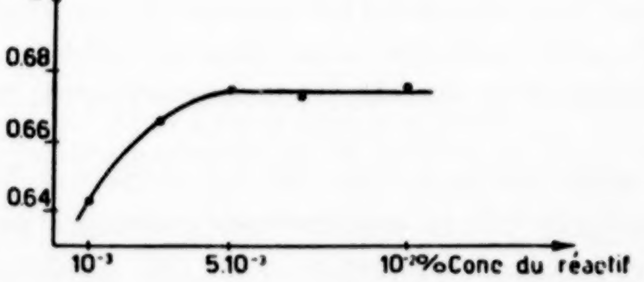

Fig. 2. Influence de la concentration du réactif

Le résultat est représenté dans la Fig. 2 pour la solution vanadique la plus concentrée ($10^{-3}\%$). L'extinction atteint une valeur constante à partir d'une concentration du réactif de $5 \cdot 10^{-3}\%$. Il en est de même pour les solutions moins concentrées de vanadium. Pour les plus basses concentrations la coloration se développe lentement et atteint une valeur stable après 30 à 40 min. Un excès du réactif étant sans influence sur la coloration, on emploiera de préférence une solution à $10^{-2}\%$.

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Influence de la température

L'extinction d'une même solution de vanadium (10^{-3}%) mesurée à 3 températures différentes, respectivement 17°, 21° et 25° C, augmente de 1.3% entre 17° et 21°, et de 1.2% entre 21° et 25°.

Le développement de la coloration est également accéléré par l'élévation de la température. En préparant les solutions à la température de 50° C dans un thermostat et en chauffant pendant 10 min à la même température, on obtient immédiatement une extinction constante, même pour les solutions à basse concentration.

Il fut trouvé qu'une variation de la température entre 50° et 55° C n'influence pas les résultats. La durée de chauffe d'autre part peut être réduite à 5 min pour la température de 55° C.

Influence d'autres ions

D'après HOSTE[1] il n'y a que les ions oxydants qui gênent la détection du vanadium par la diphénylbenzidine. Outre ces oxydants, tous les ions ayant une coloration propre, absorbant de façon appréciable dans la région d'onde de 480 mμ pourront gêner le dosage spectrophotométrique du vanadium.

L'étude de l'influence des différents ions a été limitée aux éléments ordinairement rencontrés dans les aciers. Ces éléments ont été ajoutés préalablement à la solution de vanadium en quantités variables, le rapport $C_X : C_V$ étant respectivement 1:1, 10:1 et 100:1.

L'extinction mesurée est comparée à celle obtenue avec la solution pure de vanadium de même concentration. La même solution du réactif est employée dans toutes les expériences. Les résultats sont reproduits dans le Tableau II.

TABLEAU II

VARIATION DE L'EXTINCTION E D'UNE SOLUTION DE VANADIUM EN PRÉSENCE D'AUTRES IONS. $E_0 = 0.300$

Elément ajouté	*Rapport $C_X : C_V$*		
	1 : 1	*10 : 1*	*100 : 1*
Cu^{+2}	0.306	0.321	0.840
Fe^{+3}	0.302	0.317	0.662
Ni^{+2}	0.303	0.305	0.308
Co^{+2}	0.301	0.302	—
Cr^{+3}	0.296	0.298	0.310
Cr^{+6}	coloration bleue		
Mn^{+2}	0.304	0.306	0.315
Mo^{+6}	0.304	0.287	préc. blanc
W^{+6}	0.295	0.156	coloration verte.

CONDITIONS DÉFINITIVES POUR LE DOSAGE DU VANADIUM EN SOLUTION PURE

La solution contenant le vanadium sous forme de vanadate est mélangée immédiatement avant l'emploi avec un volume égal d'acide acétique pur, exempt d'impuretés réductrices. La solution du réactif est préparée par dissolution de la diphénylbenzidine dans l'acide acétique par chauffage au bain-marie. La même solution ne sera jamais employée au-delà d'une semaine mais renouvelée de préférence tous les

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3 jours. Les solutions inconnues de vanadium et les solutions standards seront traitées par la même solution du réactif. On travaille à température constante pour toutes les solutions mesurées.

Mode opératoire

A 10 ml (pipette jaugée) d'une solution fraîche de diphénylbenzidine à $10^{-2}\%$ dans l'acide acétique, dans un tube à essai sec, on ajoute 1 ml (micropipette jaugée) de la solution vanadique à analyser. On agite pendant 2 min et on remplit une cellule colorimétrique sèche de 1 cm d'épaisseur avec la solution colorée. L'extinction est mesurée pour la longueur d'onde de 480 mμ, par rapport à un essai à blanc, composé de 10 ml de la solution du réactif et de 1 ml d'un mélange HAc : eau = 1 : 1. On attend jusqu'à ce que l'extinction soit devenue constante (5 à 10 min pour les concentrations plus élevées, 30 à 40 min pour les concentrations les plus basses).

Comme variante on peut mélanger la solution et le réactif à la température de 50° dans un thermostat. Après 10 min on refroidit, on transvase dans la cellule colorimétrique et on mesure l'extinction qui est pratiquement constante.

Loi de Beer et droite de dosage

La loi de Beer a été vérifiée pour 2 solutions différentes du réactif. Les résultats reproduits dans la Fig. 3 montrent que la loi s'applique pour les concentrations de vanadium comprises entre 10^{-4} et $10^{-3}\%$ dans la solution initiale, ce qui correspond à des quantités de vanadium de 1 à 10 γ/ml.

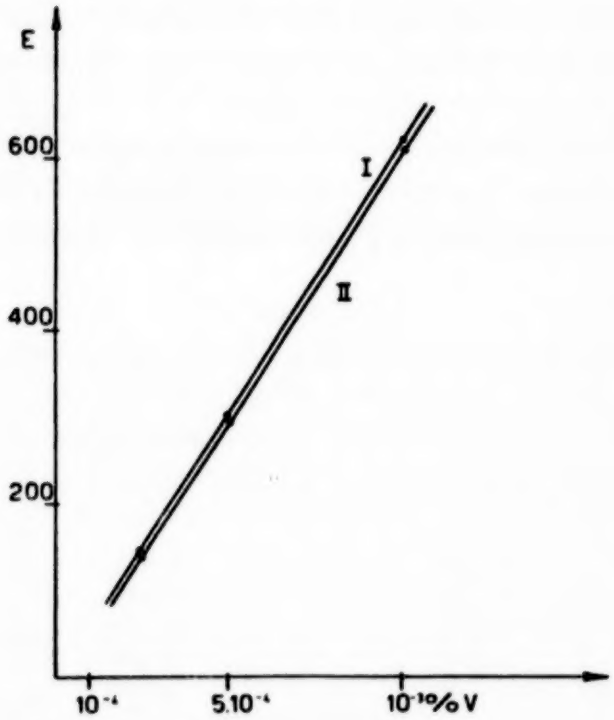

Fig. 3. Courbes de dosage

L'extinction moléculaire dépend de la qualité du réactif employé et de sa préparation. Pour les deux solutions employées ici nous trouvons comme valeur moyenne respectivement $\varepsilon_{I} = 3060$ et $\varepsilon_{II} = 3030$.

Le déplacement des droites l'une par rapport à l'autre montre l'importance de mesurer les solutions inconnues et les solutions standards avec la même solution du réactif.

Reproductibilité des mesures

La reproductibilité des mesures a été déterminée d'une part au moyen d'une solution de vanadium à $5 \cdot 10^{-4}\%$, mesurée 10 fois avec la même solution du réactif, d'autre part au moyen d'une solution de vanadium à 10^{-3} %, mesurée 10 fois avec une solution du réactif chaque fois fraîchement préparée, dans des conditions identiques. Les résultats sont résumés dans le Tableau III.

TABLEAU III

REPRODUCTIBILITÉ DES MESURES

	Solution fraîche du réactif		*Même solution du réactif*	
Expérience	*Extinction*	*Déviation avec E_M*	*Extinction*	*Déviation avec E_M*
1	0.621	0.003	0.304	0.003
2	0.612^5	0.005^5	0.302	0.001
3	0.618^5	0.000^5	0.301	—
4	0.614	0.004	0.300	0.001
5	0.636	0.018	0.301	—
6	0.620^5	0.001^5	0.303	0.002
7	0.622	0.004	0.299	0.003
8	0.614	0.004	0.300	0.001
9	0.614^5	0.003^5	0.304	0.003
10	0.609	0.009	0.300	0.001
Moyenne	0.618	0.005	0.301	0.001^4

Ces résultats indiquent que la précision est très satisfaisante pour la concentration examinée. Ils sont comparables à ceux obtenus récemment par d'autres méthodes, décrites par Wise et Brandt[4] et par Tanaka[5].

APPLICATION AU DOSAGE DU VANADIUM DANS L'ACIER

La plupart des éléments rencontrés dans les aciers gênent le dosage du vanadium lorsque le rapport X : V devient supérieur à 10 : 1. Il est dès lors absolument nécessaire de séparer le vanadium des autres éléments.

Une méthode très appropriée est l'électrolyse sur cathode de mercure décrite par Cain[6]. On opère en milieu sulfhydrique, après évaporation de la solution en présence d'acide sulfurique pour chasser les nitrates et les chlorures. Après l'électrolyse il est nécessaire d'oxyder pour s'assurer que tout le vanadium se trouve sous forme de vanadate. La durée de l'électrolyse dépend de la quantité de métal à séparer ainsi que de l'acidité de la solution. La quantité d'acide sulfurique employée est telle que la solution finale est sensiblement $1N$.

Pour les faibles teneurs en vanadium, où la prise d'essai devient plus importante, on peut séparer le vanadium de la plus grande partie du fer et du manganèse de la solution par précipitation par $NaHCO_3$ en milieu réducteur[7], laissant Fe^{+2} et Mn^{+2} en solution. Le précipité, entraînant le vanadium par coprécipitation, est remis en solution dans l'acide nitrique. Après évaporation en présence d'acide sulfurique pour chasser les nitrates, la solution est électrolysée.

L'électrolyse a lieu dans une cellule du type Melaven[8] entre la cathode de mercure de 8 cm^2 de surface et une anode de platine de 3 cm^2 de surface.

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Mode opératoire

Une quantité d'acier, 0.1 à 0.5 g, est mise en solution dans H_2SO_4 ou un mélange d'acides. On ajoute 2 ml d'H_2SO_4 — si la solution initiale n'en contient pas — et on évapore jusqu'à production de vapeurs de SO_3. On ajoute 50 ml d'eau distillée et on laisse bouillir pour dissoudre les sulfates précipités. La solution est transvasée quantitativement dans la cellule d'électrolyse. On électrolyse sous tension de 8-10 V jusqu'à décoloration complète de la solution. L'électrolyse dure de 20 à 40 min suivant l'importance de l'essai. Après séparation du mercure, la solution électrolysée est transvasée quantitativement dans un ballon jaugé de 100 ml et neutralisée à NH_3. On remplit jusqu'au trait. Une quantité adéquate de cette solution, contenant de 0.1 à 1 mg de V, est mesurée au moyen d'une pipette et transvasée dans un ballon jaugé de 100 ml. On ajoute quelques gouttes de $KMnO_4$ 0.01*N*. Après quelques minutes on chauffe à ébullition jusqu'à décoloration de $KMnO_4$. On laisse refroidir, on ajoute 50 ml d'acide acétique pur et on remplit jusqu'au trait avec de l'eau distillée. Cette solution contient alors de 1 à 10 γ de vanadium par ml. La concentration de la solution finale est déterminée en suivant le mode opératoire décrit pour la solution pure de vanadium.

Pour une prise d'essai de 0.5 g la méthode est applicable au dosage de vanadium pour des teneurs de 0.05 à 5%.

Pour des teneurs inférieures à 0.05%, on peut augmenter la prise d'essai et appliquer une séparation préalable du fer et du vanadium par la méthode au $NaHCO_3$ en milieu réducteur.

Nous avons indiqué ci-dessous les résultats obtenus pour un acier au Cr-Ni (18/8), contenant 0.5% de V et de petites quantités de Cu, Mo, Mn, Co et W variant de 0.05 à 0.5%.

Dosage du vanadium dans l'acier

Électrolyse directe (prise de 0.4 g): 0.49—0.475—0.48—0.48%.
Électrolyse après séparation préalable (prise de 1 g): 0.47—0.46%.

Il est probable que la coprécipitation incomplète du vanadium est responsable pour les résultats trop faibles, obtenus après séparation préalable par la méthode au $NaHCO_3$.

La méthode n'est pas applicable aux aciers contenant du tungstène, dès que le rapport W : V est supérieur à 1 : 1.

RÉSUMÉ

Le dosage spectrophotométrique du vanadium à l'aide d'une solution de diphénylbenzidine dans l'acide acétique a été étudié. La méthode est basée sur la réaction entre les ions V^{+5} et le réactif donnant lieu à une coloration jaune très sensible pour des solutions à faible concentration en vanadium.

L'influence de plusieurs facteurs a été examinée: nature du solvant pour le réactif; concentration des solutions de vanadium et du réactif et rapport des volumes mélangés; stabilité des solutions employées; excès de réactif; température; ions étrangers.

Dans les conditions déterminées les résultats sont reproductibles. La loi de Beer est vérifiée entre les limites de 10^{-4} à 10^{-3}% de vanadium dans la solution initiale.

La méthode a été appliquée avec succès au dosage du vanadium dans l'acier après séparation des autres éléments par électrolyse sur cathode de mercure.

SUMMARY

The spectrophotometric determination of minute amounts of vanadium with a solution of diphenylbenzidine in acetic acid has been examined. A method is developed, based on the yellow coloration which is formed when V^{+5}, in very dilute solutions, reacts with diphenylbenzidine.

The effects of various factors have been investigated: the kind of solvant used, concentrations of solutions, stability of solutions, amount of reagent, temperature, pH and diverse ions.

Beer's law is obeyed within the limite of 10^{-4}% and 10^{-3}% of vanadium. The precision is very satisfactory.

The method has been applied to the determination of vanadium in steels. Interfering ions are advantageously eliminated by electrolysis on a mercury cathode.

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ZUSAMMENFASSUNG

Die spektrophotometrische Bestimmung von Vanadin mit Diphenylbenzidin in essigsaurer Lösung wurde untersucht. Die Methode gründet sich auf die gelbe Farbe welche bei der Reaktion von V^{+5}-Ionen in sehr verdünnter Lösung mit diesem Reagenz entsteht.

Der Einfluss folgender Faktoren wurde untersucht: Art des Lösungsmittels, Konzentration und Haltbarkeit der Lösungen, Überschuss an Reagenz, Temperatur, pH und fremde Ionen.

Die Extinktion folgt dem Beer'schen Gesetz für Konzentrationen von $10^{-4}\%$ bis $10^{-3}\%$ Vanadin. Die Genauigkeit ist sehr befriedigend.

Das Verfahren wurde zur Bestimmung von Vanadin in Stahl angewendet, nachdem störende Ionen durch Elektrolyse an einer Quecksilber-Kathode beseitigt worden waren.

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THE DETERMINATION OF ORGANIC BASES WITH HEXANITRODIPHENYLAMINE

PART II. THE DETERMINATION OF PYRIDINE WITH SPECIAL REFERENCE TO THE DETERMINATION OF PYRIDINE IN ALCOHOL

by

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In a previous paper[1] it was shown that, under suitable conditions, a yellow dioxane solution of 2,2′,4,4′,6,6′-hexanitrodiphenylamine (= HNDA) was turned orange or red on the addition of pyridine through the dissociation of the acid, giving red anions. This reaction is sufficiently sensitive to permit colorimetric determination of pyridine.

Pyridine is generally determined by direct titration with standard acid or by back-titration with alkali in aqueous solution using methyl orange as the indicator. A volumetric determination of pyridine in non-aqueous media was suggested by PALIT[2], in a mixture of solvents containing glycol and higher alcohols or chloroform, and by FRITZ[3] using benzene, chlorobenzene, nitrobenzene, chloroform or petroleum ether as solvent and titrating with perchloric acid in glacial acetic acid. Both these authors used either the potentiometric method or indicators. In a similar environment a high frequency oscillometer proved suitable for the determination of pyridine[4]. Pyridine has been estimated gravimetrically as its chloraurate, its chloroplatinate and as its perchlorate[5,6]. For a colorimetric determination of pyridine various reactions have been proposed: the reaction with cyanogen bromide producing the red colour of glutaconic aldehyde[7]; the reaction with cyanogen bromide and benzidine hydrochloride[8]; the conversion of pyridine into 4-pyridyl-pyridinium dichloride[9]; colour tests with sodium in ethanol in a chloroform-water mixture[10]; the Fujiwara reaction[11] and the reaction with barbituric acid[12]. Pyridine was further determined spectrophotometrically in the ultraviolet region either after extraction with dilute phosphoric acid[13] or directly[14]. Infrared spectroscopy[15] as well as chromatography[16] have also been suggested for the quantitative analysis of pyridine.

EXPERIMENTAL

Reagents

The HNDA was an Eastman Kodak reagent for laboratory use and was not recrystallized. The dioxane, the pyridine and absolute ethyl alcohol were B.D.H. redistilled reagents.

0.1 *M* and 0.01 *M* solutions of HNDA were prepared by dissolving the yellow crystals in dioxane. Fresh solutions were always used, since these solutions are unstable, turning appreciably orange in 24 hours.

For the preparation of the calibration curve 0.05% w/v and 0.5% w/v solutions of pyridine in dioxane were used, and for the determination of pyridine in ethyl alcohol (denatured alcohol) a 0.5% v/v pyridine in 95% ethyl alcohol solution was used.

Apparatus

A Beckman DU spectrophotometer with 10 mm glass cells was used for the developmental work. The method was tested employing an E.E.L. portable colorimeter using 10 mm cells and a green filter. No other special equipment was needed.

DEVELOPMENT OF METHOD

The absorption curve of a dioxane solution of HNDA containing pyridine has already been described[1]. The method given here is based on the extreme colour sensitivity, the rapidity and the simplicity with which the coloured system is formed between HNDA and pyridine.

Optimum wavelength. Preliminary examination of the absorption curves of HNDA in the presence of different amounts of pyridine and in the absence of them, showed that the most practicable wavelength for the determination of pyridine directly was to make use of the absorbancy values between 510-550 mμ.

Preparation of the calibration curves. In order to prepare calibration curves two series of experiments were carried out. The first to determine the absorption of an amount of pyridine lying between 0.1 and 1 mg, and the second to determine that between 1 and 10 mg. In both cases the general composition of the solutions was identical: 8 ml of an HNDA solution in dioxane + (2-x) ml dioxane + x ml of a dioxane solution of pyridine. For the first set of experiments a 0.1*M* HNDA solution and a 0.05% w/v pyridine solution in dioxane were used, and for the second set a 0.01*M* HNDA solution and a 0.5% w/v pyridine solution in dioxane. The amount x of both pyridine solutions in dioxane varied from 0.0 to 2.0 ml corresponding to the amounts of pyridine mentioned above. A new calibration curve was prepared whenever a new solution of HNDA was used. The pyridine solution was added from a 1 ml graduated pipet.

Validity of Beer's law. The first calibration curve obeyed Beer's law in its total course, while with the second the calibration curve only followed the law up to 80% linearly (compare the curve in Fig. 1) while higher up some departure from the linearity was obtained.

Stability of colour. An orange or red colour appeared immediately after adding pyridine to the yellow solution of HNDA. The colour was stable for at least 6 hours.

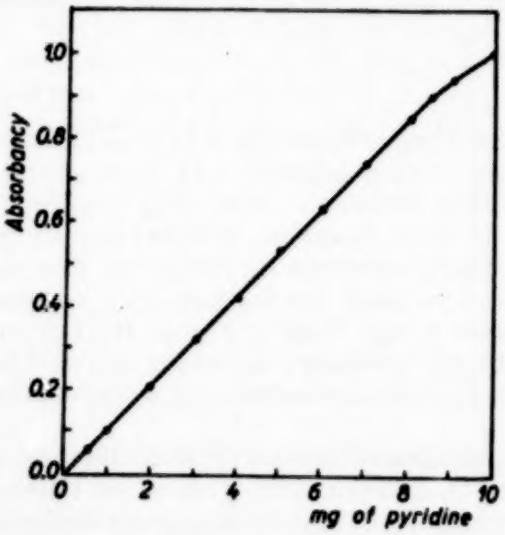

Fig. 1. Calibration curve for the determination of pyridine in denatured alcohol.

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Since the yellow solution of HNDA in dioxane itself, turned appreciably orange in 24 hours it was found desirable to prepare the calibration curve simultaneously with the unknown and to keep them under the same conditions. When the amounts of pyridine to be determined were larger, it was possible to use an aged solution of HNDA in dioxane; the differences between the colours (weak orange and red) being sufficient. In this case the HNDA solution was usable for two weeks or more.

Sensitivity. The identification limit found was $4\ \gamma$; the concentration limit was $10\ \gamma$/ml (10 p.p.m.) and the dilution limit was 10^5.

Influences and interferences. The influences of different solvents were investigated and it was found that benzene, carbon tetrachloride, chloroform and ethyl ether did not interfere with the method. Ethanol, methanol and acetone do not influence the results if present below 20%. Water has no influence if present below 10%, in cases where large amounts of pyridine are to be determined, but in cases where small amounts of pyridine are to be measured, more than 5% water may interfere. Inorganic and organic bases interfere in any amount.

Calibration curve for the determination of pyridine in denatured alcohol. Generally the pyridine content in ethanol is about 0.5% v/v. The method described permits the determination of pyridine in quantities of this order of magnitude and this procedure was adopted for its determination.

The calibration curve, shown in Fig. 1, identical with the second calibration curve described previously, permits the determination of pyridine in concentrations as low as 0.1% v/v with high accuracy. The solutions prepared in order to obtain the calibration curve had the composition: 5 ml 0.01 M HNDA in dioxane + 3 ml dioxane + $(2-x)$ ml of 95% ethyl alcohol + x ml of a 0.5% v/v pyridine solution in 95% ethyl alcohol. By plotting the absorbance readings, after subtracting the absorbance value of the blank solution (2 ml of 95% ethyl alcohol without pyridine in 10 ml volume) against their corresponding amounts in milligrams, the curve shown in Fig. 1 was obtained at 535 mμ.

RECOMMENDED METHODS

Detection of pyridine. An HNDA reagent in dioxane is suitable for the detection of amounts of pyridine as minute as $4\ \gamma$ in 8 drops of total volume, using a minimum of 5 drops of a 0.1 M solution of HNDA. Working on a spot plate even smaller amounts of pyridine are appreciable ($2\ \gamma$ in a total of 2 drops).

Determination of pyridine

A. Amounts of pyridine above 1 mg. Weigh out 0.22 g of HNDA and dissolve in 50 ml dioxane (about 0.01 M solution). To 8 ml of this solution add 2 ml of the unknown solution containing the pyridine to be determined. For solutions containing pyridine in higher concentrations than the limit given above, dilute it with dioxane. Simultaneously prepare the calibration curve as described previously under DEVELOPMENT OF METHOD. For measurements either a spectrophotometer or a colorimeter may be used. In the last case a green filter should be used.

B. Amounts of pyridine under 1 mg. Take 2.2 g of HNDA and dissolve in 50 ml dioxane. This solution which must be freshly prepared is about 0.1 M. The composition of the solution to be measured is as above and the measurements are to be carried out on a spectrophotometer at about 540 mμ.

Determination of pyridine in denatured alcohol. Use a dioxane solution of about 0.01 M concentration. To 5 ml of the HNDA solution add 3 ml more dioxane and 2 ml of the denatured alcohol. Simultaneously prepare the calibration curve as described; use a spectrophotometer or a colorimeter. Methyl alcohol and water, both commonly present in denatured alcohol to the extent of 2.5% and 5% respectively, do not interfere.

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SUMMARY

Under suitable conditions hexanitrodiphenylamine and pyridine react to form the red-coloured anion of the acid hexanitrodiphenylamine. Photometric comparison with standards permits the determination of pyridine in a concentration as low as 10 γ/ml. The method is simple and highly sensitive, but not specific. The method described has been applied to the determination of pyridine in denatured alcohol.

RÉSUMÉ

Dans des conditions déterminées, l'hexanitrodiphénylamine réagit avec la pyridine pour former l'anion de l'acide hexanitrodiphénylamine dont la coloration est rouge. Par comparaison photométrique avec une solution étalon, il est possible de doser la pyridine pour des concentrations allant jusqu'à 10 γ/ml. La méthode est simple, très sensible, mais pas spécifique. La méthode décrite a été appliquée au dosage de la pyridine dans l'alcool dénaturé.

ZUSAMMENFASSUNG

Hexanitrodiphenylamin und Pyridin reagieren zusammen unter bestimmten Bedingungen um das rot gefärbte Anion der Hexanitrodiphenylaminsäure zu ergeben. Durch photometrischen Vergleich mit Standardlösungen ist Pyridin noch in einer Konzentration von 10 γ/ml bestimmbar. Die Methode ist einfach, hochempfindlich aber nicht spezifisch. Die beschriebene Methode wurde zur Bestimmung von Pyridin in denaturiertem Alkohol angewendet.

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THE COLORIMETRIC DETERMINATION OF SECONDARY AMINES

by

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Methods for the analysis of mixtures of primary, secondary and tertiary amines usually depend on differences in reactivity towards nitrous acid[1,2] and acylating agents[3]. In these, secondary amines are generally determined by difference, and such methods are therefore unsuitable for the estimation of small quantities of secondary amines in presence of large amounts of the others. A polarographic method[4] has been devised for the determination of small quantities of dimethylamine in aqueous solutions containing the other two methylamines and ammonia; this involves preliminary treatment of the mixture with nitrous acid and separation of the dimethylnitrosamine by distillation. The necessity for removal of the nitrosamine has been eliminated in a modified procedure[5], but under these conditions unreliable results are obtained in presence of a large excess of the related bases. Other methods for the estimation of traces of secondary amines involve conversion to the dialkyl dithiocarbamate[6] and measurement of the colour intensity of the solution of its copper salt[7], but in presence of large amounts of ammonia and primary amines this procedure does not give satisfactory results. Lower monoalkylamines can be separated from the corresponding dialkylamines to eliminate interference from the former[8,9].

FEIGL AND ANGER[10] found that many secondary amines react in alkaline solution with sodium nitroprusside and acetaldehyde to give a violet-blue compound of unknown structure. In the present paper, it is shown that, under carefully controlled conditions, this colour reaction may be used for the quantitative determination of small amounts of certain dialkylamines, and the estimation can be carried out in presence of primary and tertiary amines and of ammonia.

EXPERIMENTAL

(a) *Reagents and apparatus*

The reagent solutions were prepared from AnalaR sodium nitroprusside and freshly distilled acetaldehyde. These were stable for about two weeks when kept in well-stoppered bottles at 0-5° C. Solutions of AnalaR borax and sodium carbonate were used to adjust pH.

All secondary amines, ethylamine and triethylamine were purified by repeated fractionation of the best available commercial samples. Methylamine and trimethylamine were purified by recrystallization of their hydrochlorides from chloroform and ethyl alcohol respectively. AnalaR

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ammonia (s.g. 0.880) was used without further purification. Solutions of the amine hydrochlorides and ammonium chloride were prepared by distillation of the free bases into standard hydrochloric acid. The concentration of the free base was determined by back-titration of the excess acid against standard alkali with methyl orange-xylene cyanol as indicator.

Optical densities were measured with reference to blank reagent solutions in 1 cm-cells in a Unicam SP 500 spectrophotometer.

(b) *Influence of reagent concentrations*

The optimum conditions for the determination were investigated with dimethylamine. The development of the colour is markedly dependent on pH which for maximum sensitivity must lie between 9.6 and 10.2 [Fig. 1 (a)], and is also influenced by the concentration of sodium nitroprusside, which should lie between 1.0 and 1.5% w/v [Fig. 1 (b)]. The acetaldehyde concentration is less critical, but the reagent should contain not less than 10% v/v of the aldehyde [Fig. 1 (c)].

In all subsequent determinations, therefore, the reagent solution contained 1.0% w/v of sodium nitroprusside and 10% v/v of acetaldehyde, and the colour was allowed to develop in a solution of pH 9.8.

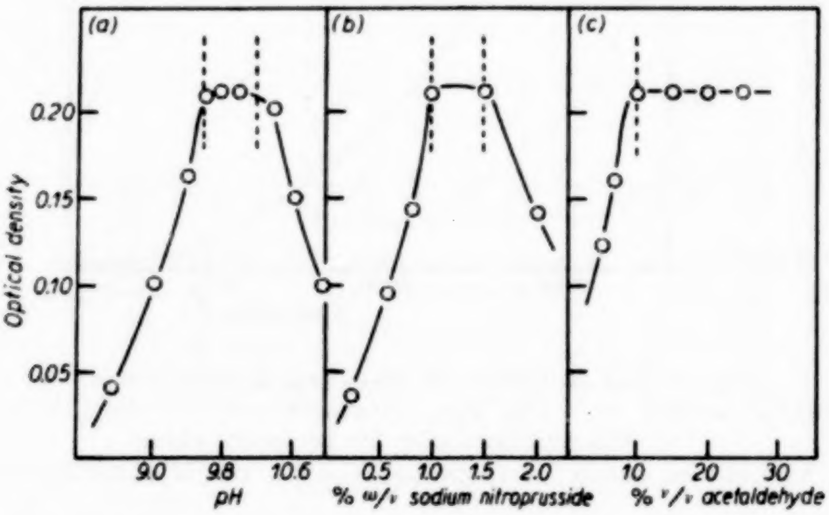

Fig. 1. The influence of pH and reagent concentrations on absorption. [Dimethylamine] = $1.60 \cdot 10^{-3} M$, λ = 5650 Å.
(a) [Sodium nitroprusside] = 1.0% w/v, [Acetaldehyde] = 10% v/v, pH varied.
(b) [Acetaldehyde] = 10% v/v, pH = 9.8, [Sodium nitroprusside] varied.
(c) [Sodium nitroprusside] = 1.0% w/v, pH = 9.8, [Acetaldehyde] varied.

(c) *Procedure*

20-ml portions of a buffer solution containing 9.53 $g.l^{-1}$ borax and 5.30 $g.l^{-1}$ sodium carbonate are placed in two 100-ml lipped beakers, and 5-ml portions of the reagent solution are added. 5 ml of distilled water and 5 ml of the sample respectively are run into the two beakers and the time is taken. The wavelength for maximum absorption varies slightly with the different dialkylamines, but with the compounds studied lies in the region: 5600-6000 Å. The optical densities are compared after times depending on the nature of the secondary amine (see below).

RESULTS

Dimethylamine

The coloured compound formed with dimethylamine has maximum absorption at 5650 Å (Fig. 2). The colour develops rapidly when the reactants are first mixed; subsequently the optical density increases more slowly and over a considerable period the log I_0/I — time plot is accurately linear (Fig. 3). The optical density does not reach a constant value within a reasonable time, but it was shown that reproducible results are obtained by making measurements after twenty minutes' development time. In practice, since the colour is still developing rapidly at this stage, the optical density should be measured at frequent intervals between fifteen and twenty-five minutes and its value after twenty minutes deduced by interpolation.

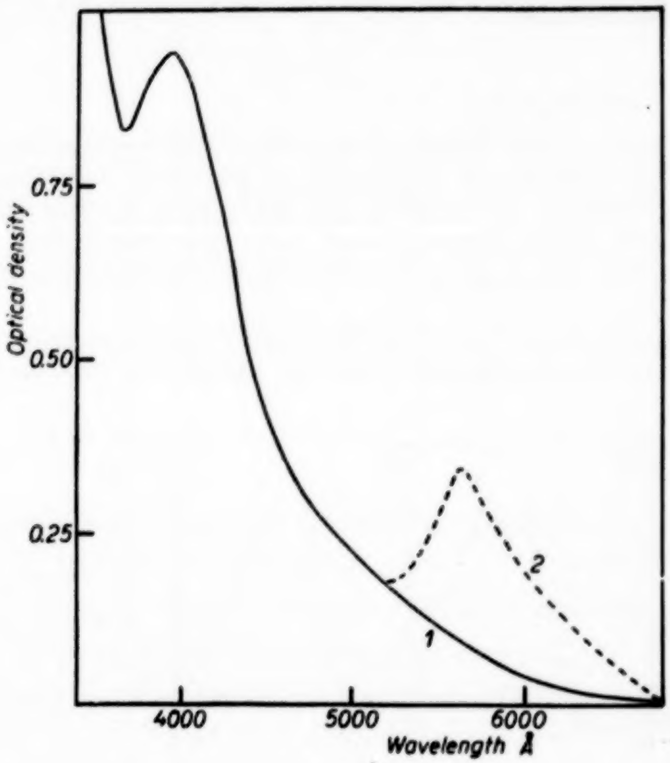

Fig. 2. The influence of wavelength on absorption.
[Sodium nitroprusside] = 1.0% w/v, [Acetaldehyde] = 10% v/v, pH = 9.8.
1. Absorption curve for reagents alone.
2. Absorption curve for reagents + 2.5 · $10^{-3}M$ dimethylamine.

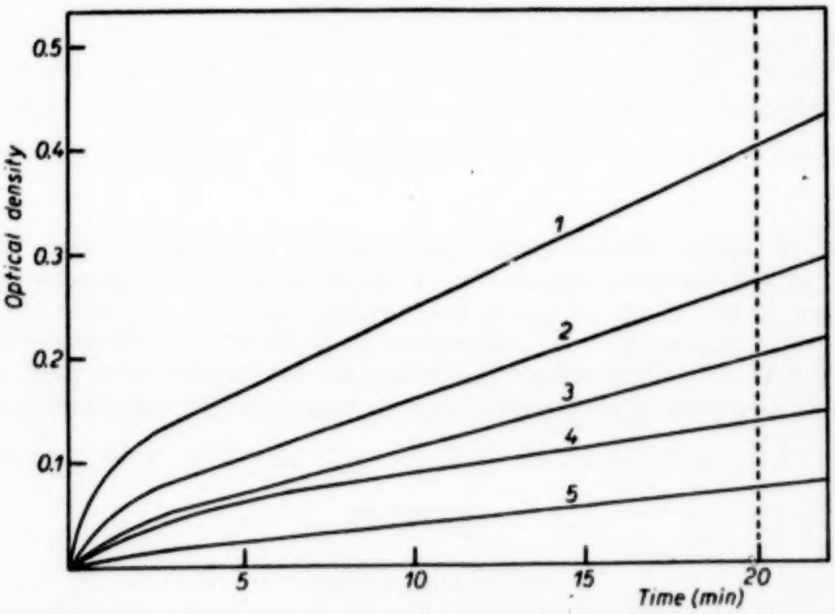

Fig. 3. The development of colour with time for dimethylamine and diethylamine.
[Sodium nitroprusside] = 1.0% w/v, [Acetaldehyde] = 10% v/v, pH = 9.8, λ = 5650 Å.
1. [Dimethylamine] = 3.01 · $10^{-3}M$.
2. [Dimethylamine] = 2.01 · $10^{-3}M$.
3. [Dimethylamine] = 1.51 · $10^{-3}M$.
4. [Diethylamine] = 4.70 · $10^{-3}M$.
5. [Diethylamine] = 2.60 · $10^{-3}M$.

Under these conditions, Beer's law is obeyed for concentrations of dimethylamine up to $3.0 \cdot 10^{-3}$ mole.l^{-1} [Fig. 4(a)], and the colour is unaffected by the presence of ammonia, methylamine and trimethylamine (Table I).

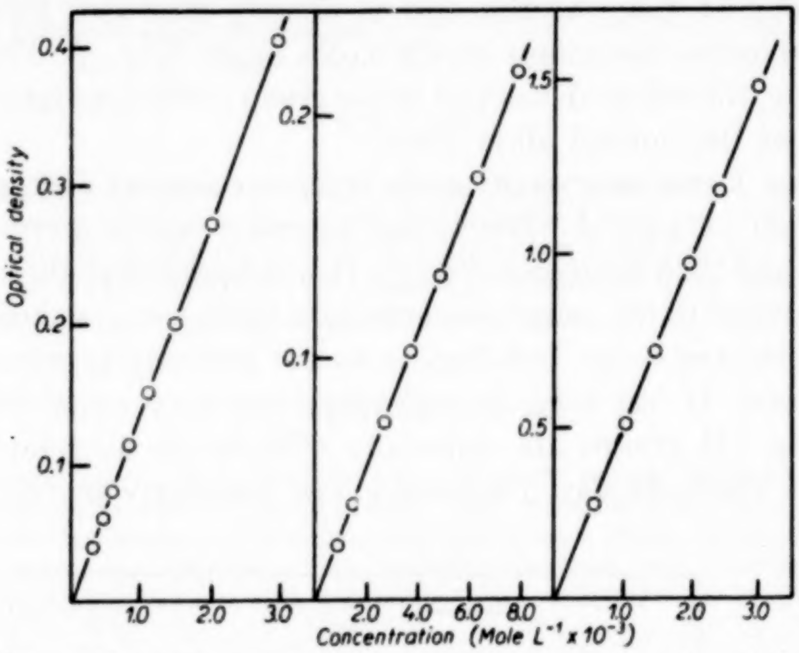

Fig. 4. The influence of amine concentration on absorption.
[Sodium nitroprusside] = 1.0% w/v, [Acetaldehyde] = 10% v/v, pH = 9.8.
(a) Dimethylamine, λ = 5650 Å.
(b) Diethylamine, λ = 5650 Å.
(c) Di*iso*butylamine, λ = 5900 Å.

TABLE I

THE DETERMINATION OF DIMETHYLAMINE IN PRESENCE OF AMMONIA AND OTHER METHYLAMINES

Moles per litre × 10⁻³ (present)				*Moles per litre × 10⁻³ (found)*
Ammonia	Methylamine	Trimethylamine	Dimethylamine	Dimethylamine
2.16	—	—	0.58	0.59, 0.61
3.36	—	1.08	1.16	1.16
3.36	1.90	3.77	—	none found
3.36	10.43	0.76	1.16	1.16, 1.13
5.72	0.95	1.89	0.23	0.23, 0.22
9.88	1.23	—	0.80	0.81
—	—	2.26	0.58	0.59
—	6.26	1.13	1.51	1.51

Diethylamine

Diethylamine under similar conditions gives a less intense colour than dimethylamine, and this also has maximum absorption at 5650 Å. The colour develops with time in the same way as with dimethylamine (Fig. 3), and the optical density may again be conveniently measured after twenty minutes. Beer's law is obeyed for concentrations up to $8.0 \cdot 10^{-3}$ mole.l^{-1} [Fig. 4(b)]. The colour is uninfluenced by the presence of even a large excess of ethylamine and triethylamine.

Higher dialkylamines

The behaviour of some higher aliphatic secondary amines was also investigated. Di-*n*-propylamine, di-*n*-butylamine and di-*n*-amylamine form compounds with absorption maxima at 5800 Å. The optical density increases rapidly at first but after about 6-8 minutes the colour slowly fades again (Fig. 5). From diethylamine to di-*n*-amylamine, the colour developed under given conditions increases in intensity with the length of the normal alkyl chain.

Di*iso*butylamine forms an exceptionally intense coloured compound with an absorption maximum at 5900 Å. The colour intensity again increases rapidly to a maximum value and then decreases (Fig. 5). It was found that the maximum optical density is proportional to the amine concentration up to 3.0×10^{-3} mole·l^{-1} [Fig. 4(c)].

Di*iso*propylamine and di-*sec.*-butylamine do not give any appreciable colour under the conditions used. It has been shown[3] that secondary amines with the nitrogen atom attached to CH groups are unusually difficult to acetylate. It is precisely such compounds which display abnormally low reactivity in the present system.

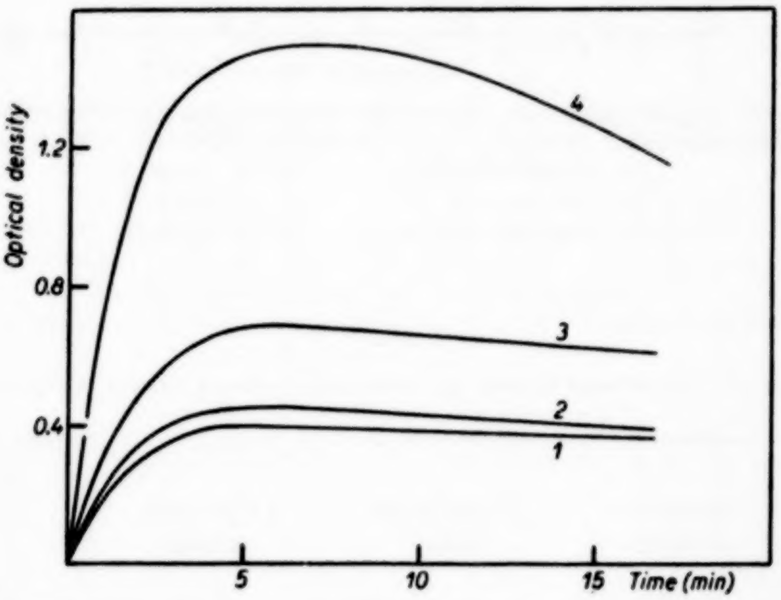

Fig. 5. The development of colour with time for higher dialkylamines.
[Sodium nitroprusside] = 1.0% w/v, [Acetaldehyde] = 10% v/v, pH = 9.8, [Amine] = $3.0 \cdot 10^{-3} M$.

(1) Di-*n*-propylamine, λ = 5800 Å.
(2) Di-*n*-butylamine, λ = 5800 Å.
(3) Di-*n*-amylamine, λ = 5800 Å.
(4) Di*iso*butylamine, λ = 5900 Å.

CONCLUSIONS

Under carefully controlled conditions, the colour reactions described may be used to give quick and reliable results for the quantitative analysis of small amounts of specific dialkylamines. The instability of the coloured compound constitutes a disadvantage, but the method is particularly valuable for the estimation of secondary amines in presence of related bases, as it can be used without initial separation of the constituents. The reproducibility is found in general to be within ±4% over the range of concentrations studied.

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SUMMARY

This paper describes how, under carefully controlled conditions, an already known colour reaction may be used as the basis of a quick and accurate method for the estimation of secondary amines; the determination can be carried out in the presence of an excess of primary and tertiary amines and of ammonia. The correct conditions for maximum sensitivity of the method have been found for a number of aliphatic amines.

RÉSUMÉ

Les auteurs démontrent comment, dans des conditions déterminées, une réaction colorée déjà connue, peut servir de base à une méthode rapide et précise pour le dosage des amines secondaires. Cette détermination peut s'effectuer en présence d'un excès d'amines primaires, d'amines tertiaires et d'ammoniaque. Les conditions nécessaires pour obtenir une sensibilité maximum ont été établies pour quelques amines aliphatiques.

ZUSAMMENFASSUNG

In der vorliegenden Arbeit wird beschrieben, wie unter genau eingehaltenen Bedingungen eine schon bekannte Farbreaktion zur schnellen und genauen Bestimmung von sekundären Aminen verwendet werden kann. Die Bestimmung kann ebenso in der Anwesenheit von primären und tertiären Aminen, sowie Ammoniak, durchgeführt werden. Für eine Anzahl aliphatischer Amine sind die Bedingungen, welche eine maximale Empfindlichkeit der Methode gewährleisten, ermittelt worden.

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A DIRECT MICROHETEROMETRIC DETERMINATION OF PALLADIUM WITH α-NITROSO-β-NAPHTHOL IN EXCESSES OF FOREIGN METALS. A STUDY OF THE REACTION AND THE WORKING CONDITIONS

by

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INTRODUCTION

The reaction between palladium and α-nitroso-β-naphthol (= $\alpha\beta$) was studied by W. SCHMIDT[1] who proposed using it for the determination of palladium. M. WUNDER AND V. THURINGER[1] then gave the working conditions necessary for the separation of palladium from iron and copper. SCHMIDT showed that palladium can be separated from the platinum group metals with the aid of $\alpha\beta$. SCHMIDT precipitated the palladium from a boiling solution which contained large amounts of acetic acid in addition to nitric (or hydrochloric) acid. The precipitate corresponded to the formula $(C_{10}H_6ONO)_2Pd$. When iron was present, WUNDER ignited the precipitate and determined the residue as metallic palladium.

Presented here is a heterometric study of the reaction concerned and its dependence on the medium, acidity, supplementary salts and complexing agents. To study the influence of the medium, parallel experiments were carried out in aqueous and in solutions of 50% ethyl alcohol, acetone and dioxan. It was ascertained that the presence of an organic solvent was favourable and made the heterometric determination more sensitive. As to the influence of Cl^- and NO_3^- anions, it was found that, although in dilute solution both acted similarly, at a somewhat higher concentration ($\sim 0.2M$) of chloride the precipitate of palladium-$\alpha\beta$ failed to appear or appeared very late and the determination became illusory. In contrast, the reaction was entirely uninfluenced by the presence of large amounts of nitrate.

The working conditions employed in the present study were completely different from those observed in macro- or microgravimetry: the precipitation occurred at 20° C in a 50% alcoholic solution. In all titrations the first maximum density point (= end-point) was obtained at the molar ratio of 1 Pd : 3 $\alpha\beta$. The same ratio was obtained in the titrations of $PdCl_2$ with $\alpha\beta$ (in alcohol) and in the reverse titrations of $\alpha\beta$ with $PdCl_2$. It was established that the heterometric reaction between palladium and $\alpha\beta$ is of high sensitivity (concentration $1\text{-}2 \cdot 10^{-4}M$) and of the same degree as the precipitation of cobalt with $\alpha\beta$. It is about three times more sensitive than the heterometric determination of palladium with dimethylglyoxime. But the advantage of using dimethylglyoxime is that palladium can be determined heterometrically without difficulty whatever in the presence of large excesses of copper ($\sim 99.5\%$) (see special report on determination of palladium with dimethylglyoxime which will be published soon).

A red filter was used and, generally, the presence of large excesses ($\geqslant$ 99.5%) of foreign metals had no influence on the heterometric determination of the palladium. In some cases in the presence of coloured cations the red filter was not used or was replaced by a blue filter (Co). By maintaining the special working conditions given in this report, palladium could be determined directly in solutions containing $\geqslant$ 99.5% of each of the following cations: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Al^{+3}, Cr^{+3}, Fe^{+3}, Pb^{+2}, Cd^{+2} and Hg^{+2}. The direct determination of palladium in solutions containing excesses of copper has so far not been successful.

A study of the heterometric determination of palladium with $\alpha\beta$ in the presence of the noble metals will be presented in a special report.

Most of the titrations presented lasted about 20-25 minutes and the maximum error was about 3%. Generally the error was considerably lower and was less than 2%.

EXPERIMENTAL

The same working conditions were employed as in previous investigations[2]. A red filter was used in titrations of colourless solutions. In the presence of coloured foreign salts the results were more reliable and higher densities were obtained when no filter whatever was used. With cobalt, when no filter (or a red filter) was used, no end-point could be reached and the densities rose beyond the calculated end-point. Good results were obtained using a blue filter (Fisher S.C.).

The reaction vessel had a diameter of 3.6 cm. The volume of the solution titrated was always 20 ml and the reaction temperature was 20° C.

The reagents used were all either analytical reagents or chemically pure.

The $\alpha\beta$ was a BDH pure reagent. A stock solution of $\alpha\beta$ was obtained by weighing the calculated amount of $\alpha\beta$ and dissolving in distilled alcohol ($\sim$ 95%). More dilute solutions of $\alpha\beta$ were obtained by adding alcohol to the calculated amount of the stock solution. The $\alpha\beta$ solutions were kept in dark brown bottles. The $PdCl_2$ used was a BDH pure reagent. An $0.01\,M$ stock solution was prepared by weighing the necessary amount of the salt and dissolving it in water acidified with HCl. The $0.01\,M$ $PdCl_2$-stock solution was $0.25\,M$ in HCl. The more dilute $PdCl_2$ solutions were prepared by adding water to the calculated amount of the stock solution.

In all heterometric titrations the end-point of the reaction was obtained, from the intersection of two lines, by drawing enlarged density curves. A line was drawn through the density points, in approximately the last quarter of the titration curve. Another line was drawn through the maximum density points. The intersection point (= x) of both lines is the end-point. In a few cases, the first contact point (= c) of the titration curves with the maximum density line was taken instead.

RESULTS AND DISCUSSION

Tables I and II present a selection of experiments made and the results obtained. Table I presents experiments carried out in the absence of foreign metals whilst Table II shows results obtained with palladium in the presence of large excesses of foreign metals.

In neutral aqueous solutions. In the absence of supplements (exps. 1-3) the sensitivity of the reaction was low, even when a maximum amount of palladium was present (exp. 1). The maximum density values obtained in exps. 2 and 3 are apparently independent of the molarity of the titrant.

In sodium acetate solution. The densities were higher, especially with less acetate (exps. 6 and 7).

In the presence of citrate or tartrate. The maximum density values obtained (exps. 8 and 9) were low and the results were not certain.

In ammonia-ammonium nitrate mixture. (exp. 10). The density value was low and no end-point was reached.

In sodium tetraborate. The densities increased continuously beyond the calculated end-point (exp. 11).

Influence of the medium

The influence of polar organic reagents on the reaction was studied. Parallel experiments were carried out in 50% solutions of alcohol, acetone or dioxan. The experiments which were carried out in the absence of supplements (compare exps. 1, 12 and 13) clearly showed that the presence of an organic solvent was favourable and the maximum density values were twice as high. How-

TABL

Composition: a ml mM $PdCl_2$ + b ml supplements + (20-a-b) ml H_2O + x ml nM αβ (alc)*

Content			
Exp. no.	*Supplements*	*$PdCl_2$*	
		Molarity	*ml*
1	H_2O	0.0033	5
2	,,	0.0033	3
3	,,	0.0033	3
4	4 ml M CH_3COOH + 1 ml M CH_3COONa	0.0033	5
5	2 ,, ,, ,, + 2 ,, ,, ,,	0.0033	5
6	1 ml M CH_3COONa	0.0033	3
7	4 ,, ,, ,,	0.0033	3
8	1 ml M Na_3-citrate + 1 ml M CH_3COONa	0.0033	3
9	1 ,, ,, K_2-tartrate + 1 ,, ,, ,,	0.0033	3
10	2 ,, ,, NH_3 + 2 ml M NH_4NO_3	0.0033	5
11	5 ,, 0.1M $Na_2B_4O_7$	0.0033	3
12	10 ml alcohol	0.0033	5
13	10 ,, acetone	0.0033	3
14	1 ml M HCl + 10 ml alcohol	0.0033	3
15	1 ,, ,, ,, + 10 ,, acetone	0.0033	3
16	1 ,, ,, ,, + 10 ,, dioxane	0.0033	3
17	3 ,, ,, ,, + 10 ,, ,,	0.0033	3
18	3 ,, ,, CH_3COOH + 10 ml dioxane	0.0033	3
19	5 ,, ,, CH_3COONa + 10 ,, ,,	0.0033	3
20	2 ,, ,, ,, + 10 ,, acetone	0.0033	3
21	5 ,, ,, ,, + 10 ,, ,,	0.0033	3
22	5 ,, 0.1M $Na_2B_4O_7$ + 10 ml acetone	0.0033	3
23	1 ,, M HCl + 10 ml alcohol	0.001	5
24	1 ,, ,, ,, + 4 ml M NH_4NO_3	0.001	5
25	1 ,, ,, HNO_3 + 10 ml alcohol	0.001	5
26	1 ,, ,, HCl + 4 ml M NH_4Cl + 10 ml alcohol	0.001	5
27	1 ,, ,, ,, + 4 ,, ,, NH_4NO_3 + 10 ,, ,,	0.001	5
28	1 ,, ,, ,, + 10 ml acetone	0.001	5
29	1 ml M HCl + 10 ml dioxane	0.001	5
30	3 ,, ,, ,, + 10 ,, alcohol	0.001	5
31	3 ,, ,, ,, + 10 ,, acetone	0.001	5
32	3 ,, ,, ,, + 10 ,, dioxane	0.001	5
33	3 ,, ,, HNO_3 + 10 ,, acetone	0.001	5
33a	3 ,, ,, ,, + 10 ,, alcohol	0.001	5

* αβ = α-nitroso-β-naphthol. ** c = contact point. *** ∞ = density increases continuously.

= 20° C. Red filter

		Found				
αβ						
Molarity	ml calc.	ml found	Initial precip. at ml	Maxim. density value	Approx. titration time in min	Error %
0.02	2.5	2.47	0.0	0.43	17	—1.0
0.01	3.1	3.0	0.0	0.26	21	0.0
0.02	1.55	1.57	0.0	0.25	15	+1.0
0.02	2.5	2.5	0.0	0.48	14	0.0
0.02	2.5	∿2.4	0.0	0.53	17	
0.01	3.1	3.10	0.0	0.68	14	0.0
0.01	3.1	3.07	0.0	0.48	18	—1.0
0.02		3.0 c**	0.0	0.22	17	
0.01	3.1	2.5	0.0	0.25	16	
0.02	2.5	∞***	0.0	>0.25	21	
0.02		∞***	0.0	>0.40	21	
0.02	2.5	2.47	0.0	0.75	17	−1.2
0.02	1.55	1.54	0.0	0.85	15	—0.6
0.01	3.1	3.06	0.0	0.89	21	—1.3
0.01	3.1	3.05	0.4	0.85	20	—1.6
0.01	3.1	3.0	0.0	1.05	23	—3.2
0.01	3.1	3.08	0.4	1.01	27	—0.7
0.01	3.1	3.0 c**	0.0	1.02	25	
0.01	3.1	3.10	0.0	0.89	26	0.0
0.01	3.1	3.10	0.0	0.75	23	0.0
0.01	3.1	3.02	0.0	0.81	27	—2.6
0.01	3.1	∞***	0.0	>0.33	26	
0.005	3.1	3.15	0.4	0.58	29	+1.6
0.005	3.1	3.13	0.0	0.19	22	+1.0
0.005	3.1	3.08	0.0	0.56	22	—0.7
0.005	3.0	∞***	1.0	>0.19	26	
0.005	3.1	3.15	0.4	0.55	22	+1.6
0.005	3.1	3.10	0.0	0.59	21	0.0
0.005	3.1	3.13	0.6	0.57	19	+1.0
0.005	3.1	3.05	0.8	0.46	28	—1.6
0.005	3.1	3.3	0.8	0.35	19	
0.005	3.1	3.07	1.0	0.54	20	—1.0
0.005	3.1	3.25	0.4	0.67	20	
0.005	3.1	3.15	0.0	0.55	22	+1.6

TABL

Composition: a ml mM $PdCl_2$ + b ml supplements + (20-a-b) ml H_2O + x ml 0.005M $\alpha\beta$ (alc)

Content			
Exp. no.	*Supplements*	*Foreign metal mg*	*Pd %*
34	1 ml M HCl + 5 ml 2M $MgCl_2$	243.2	
35	1 ,, ,, ,, + 5 ,, 2 ,, ,, + 10 ml alcohol		
36	1 ,, ,, ,, + 5 ,, 2 ,, ,, + 10 ,, dioxane		
37	1 ,, ,, ,, + 1 ,, 1 ,, ,, + 10 ,, alcohol	24.3	2.1
38	1 ,, ,, HNO_3 + 1 ,, ,, $Mg(NO_3)_2$ + 10 ml alcohol		
39	1 ,, ,, ,, + 4 ,, ,, ,, + 10 ,, ,,	97.3	0.5
40	1 ,, ,, ,, + 4 ,, ,, $Ca(NO_3)_2$ + 10 ,, ,,	160.3	0.3
41	1 ,, ,, ,, + 1 ,, ,, $Ba(NO_3)_2$ + 10 ,, ,,	137.4	0.3
42	1 ,, ,, ,, + 4 ,, ,, $Zn(NO_3)_2$ + 10 ,, ,,	261.5	0.2
43	1 ,, ,, ,, + 4 ,, ,, $Mn(NO_3)_2$ + 10 ,, ,,	219.7	0.2
44	1 ,, ,, ,, + 4 ,, ,, $Ni(NO_3)_2$ + 10 ,, ,,	234.8	0.2
45	1 ,, ,, ,, + 4 ,, ,, ,, + 10 ,, ,,	234.8	0.1
46	1 ,, ,, ,, + 4 ,, ,, ,, + 10 ,, ,,		
47	1 ,, ,, ,, + 4 ,, ,, ,, + 10 ,, ,,	234.8	0.1
48	3 ,, ,, ,, + 1 ,, ,, $Co(NO_3)_2$ + 10 ,, ,,	58.94	0.9
49	1 ,, ,, ,, + 4 ,, ,, $Al(NO_3)_3$ + 10 ,, ,,	107.9	0.5
50	1 ,, ,, ,, + 2 ,, ,, $Cr(NO_3)_3$ + 10 ,, ,,	104.0	0.5
51	1 ,, ,, ,, + 4 ,, ,, ,, + 10 ,, ,,	208.1	0.2
52	1 ,, ,, ,, + 1 ,, ,, $Fe(NO_3)_3$ + 10 ,, ,,	55.9	1.0
53	1 ,, ,, ,, + 0.5 ,, ,, ,, + 2 ml M tartaric acid + 10 ml alcohol	27.9	1.0
54	1 ,, ,, ,, + 0.5 ,, ,, ,, + 2 ,, ,, tartaric acid + 10 ml alcohol		
55	1 ,, ,, ,, + 1 ,, ,, ,, + 2 ,, ,, tartaric acid + 10 ml alcohol	55.9	0.4
56	1 ,, ,, ,, + 1 ,, ,, ,, + 3 ,, ,, tartaric acid + 10 ml alcohol		
57	1 ,, ,, ,, + 2 ,, ,, ,, + 3 ,, ,, tartaric acid + 10 ml alcohol	111.7	0.2
58	1 ,, ,, ,, + 2 ,, ,, ,, + 4 ,, ,, tartaric acid		
59	1 ,, ,, ,, + 4 ,, ,, $Pb(NO_3)_2$ + 10 ,, alcohol	828.8	0 0
60	1 ,, ,, ,, + 4 ,, ,, $Cd(NO_3)_2$ + 10 ,, ,,	449.6	0.1
61	3 ,, ,, ,, + 1 ,, ,, $Cu(NO_3)_2$ + 10 ,, ,,	63.5	0.8
62	1 ,, ,, ,, + 5 ,, 0.2M $Hg(NO_3)_2$ + 10 ml alcohol	200.6	0.2

1) $\alpha\beta$ = α-nitroso-β-naphthol; 2) 0.002M; 3) without filter; 4) bl. = blue filter; 5) ∞ = density incre
beyond the end-point; 6) ↓ = a precipitate before the titration.

= 20° C. Red filter. Amount Pd present: 0.267-0.534 mg (conc. 1.25-2.5 · $10^{-4}M$)

		Found					
PdCl$_2$		*αβ*		*Initial precip. at ml*	*Maxim. density value*	*Titration time in min*	*Error %*
ml	*Molarity*	*ml calc.*	*ml found*				
5	0.001	3.1		∞ 5)	0.06	18	
5	0.001	3.1	∞ 5)	1.6	∞0.20 5)	38	
5	0.001	3.1		∞ 5)	0.0	15	
5	0.001	3.1	∞ 5)	0.8	>0.40	24	
5	0.001	3.1	3.06	0.0	0.59	23	−1.2
5	0.001	3.1	3.10	0.0	0.59	25	0.0
5	0.001	3.1	∼3.10	0.0	0.52	25	0.0
5	0.001	3.1	3.10	0.0	0.50	21	0.0
5	0.001	3.1	3.10	0.0	0.49	25	0.0
5	0.001	3.1	3.12	0.0	0.55	25	+0.7
5	0.001	3.1	3.2	0.0	0.51	22	+3.2
5	0.0005	3.86 2)	3.90	0.0	0.63 3)	27	+1.0
5	0.001	3.1	3.10	0.0	0.87 3)	23	0.0
5	0.0005	3.86 2)	3.78	0.4	0.34	23	−2.0
5	0.001	3.1	2.90	0.0	bl.0.68 4)	15	
5	0.001	3.1	3.05	0.0	0.59	26	−1.6
5	0.001	3.1	3.07	0.0	0.43 3)	26	−1.0
5	0.001	3.1	3.10	0.2	0.35 3)	23	0.0
5	0.001		∞ 5)	0.0	>0.52	20	
5	0.0005	3.86 2)	3.74	0.2	0.29	33	−3.0
5	0.001		?3.05	0.0	0.72 3)	22	
5	0.0005	3.86 2)	3.80	0.4	0.44 3)	29	−1.5
5	0.0005	3.86 2)	3.80	0.0	0.48 3)	26	−1.5
5	0.0005			↓ 6)			
5	0.0005	3.86 2)	?3.5	0.0	0.18 3)	24	
5	0.001	3.10	3.10	0.0	0.42	22	0.0
5	0.001	3.10	3.06	0.0	0.53	22	−1.2
5	0.001	3.1	∞ 5)	0.0	>0.80	22	
5	0.001	3.1	3.10	0.0	0.31	24	0.0

ever, the results which were obtained in the presence of a mineral acid, acetic acid or sodium acetate were safer. Therefore, most of the titrations described below were carried out in a 50% alcoholic medium acidified with a mineral acid. The difference in the effectiveness of the organic solvents used is not considerable although dioxan seems to act somewhat more favourably than the others.

Influence of the acidity

The following conclusions may be reached by comparing experiments 14-21. The titrations could be carried out with equal success in hydrochloric or acetic acid solutions or in solutions of sodium acetate, whatever the organic solvent present. The experiments in acetone with a larger amount of hydrochloric acid (exps. 31 and 33) gave the first maximum density point late and the error was large. No end-point was reached when the solutions contained borax (exp. 22).

Some experiments were carried out in order to investigate the influence of concentrated neutral salts as chlorides or nitrates. In aqueous solution the density was low in the presence of hydrochloric acid-ammonium nitrate (exp. 24). The effect was generally the same whether hydrochloric or nitric acid was used (exps. 23 and 25). But whether ammonium nitrate or ammonium chloride was added to the hydrochloric acid was of influence since entirely different results were obtained in each case, (exps. 26 and 27). In the presence of ammonium chloride the initial precipitation occurred late, the density was low and no end-point was reached.

It could be ascertained later (see Table II) that the chlorides have a deleterious effect and could not be present. This is almost certainly caused by the complex formation between palladium and chloride and the rising concentration of the chlorocomplex with increasing concentrations of chloride. In contrast, the presence of nitrates had no influence whatsoever on the results.

Titrations in the presence of foreign salts

Table II presents a selection of experiments carried out in the presence of foreign salts.

Influence of chlorides. The influence of magnesium chloride in hydrochloric acid solution was studied (exps. 34-37). In aqueous solution (exp. 34), practically no precipitation at all occurred. In 50% alcoholic solution (exps. 35 and 37) the more chloride that was present, the later the initial precipitation occurred. In both cases no end-point was reached. All further experiments were therefore made with nitrates instead of chlorides.

The sensitivity. From experiments 23-34 it may be accepted that 0.3-0.5 mg palladium in 20 ml solution (concentration $1\text{-}2 \cdot 10^{-4}M$) were sufficient for the determination either in the absence or in the presence of excesses of foreign metals. Apparently most of the foreign metals had no influence whatever on the maximum density values obtained, and the determination was carried out with an error of 0.0-2%. There are some special metals, in the presence of which, the maximum density values were higher. Thus, in the presence of nickel or iron, *if no filter at all was used*, the density values obtained were approximately twice as high as in the same experiment using a red filter. Therefore, in these cases, half the amount of palladium could be analysed with the same success.

Most of the foreign metals were present at a concentration of $0.2M$ and the molar ratio between the palladium and the foreign cation was therefore 1 : $\sim$1000. As the foreign metals did not influence the maximum density values of the standard without foreign metal present, there is no doubt that much more of the foreign metals could have been present in the analysed solutions. In the presence of iron or chromium (and Co) the concentrations quoted are the maxima which can be used.

The results obtained in the presence of excesses of iron(III), chromium(III), nickel, cobalt and copper deserve special consideration. In all other cases no difficulties were encountered. Three of these metals (cobalt, iron and copper) formed strong complex compounds with $\alpha\beta$ which were very insoluble.

Nickel. In the presence of excesses of nickel (exps. 44-47), working *without* a filter, the amount of palladium analysed (exp. 45) could be reduced and the maximum density value obtained was still high. Therefore, approximately 0.2 mg Pd was sufficient and the percentage of Pd in nickel was then about 0.05%.

Iron. Many experiments were carried out in order to determine palladium directly in excesses of ferric iron. These experiments were carried out both with and without the use of a red filter, but in all cases the density rose continuously beyond the calculated end-point. Only in the presence of excesses of tartaric acid, working *without* a filter (exps. 52-58) were definite end-points obtained. In addition, the maximum density values were high and less palladium was used. In spite of this, the percentage of palladium was still high ($\sim$ 0.5%) (exp. 55).

Chromium. In contrast to nickel and iron, in the presence of chromium the densities were somewhat reduced (exps. 50 and 51). Here, also, the titration had to be carried out without the red filter.

Cobalt. In the presence of excesses of cobalt (exp. 48) a safe end-point was obtained using a blue filter. The amount of cobalt which could be present was also restricted.
Copper. In all cases with copper the densities rose continuously beyond the calculated end-point.

Composition

In all experiments which were carried out in this work, the analytical end-point was found at the molar ratio of 1 Pd : 3 $\alpha\beta$, a fact which is very remarkable. It is unreasonable to assume that $\alpha\beta$ had any oxidizing effect on the $PdCl_2$ (contrarily to cobalt!) in the strongly acid solutions used. The compound obtained at 20° C may be presented as $Pd(\alpha\beta)_2.\alpha\beta$, although the titration curves show no sign that one molecule $\alpha\beta$ was used differently from the other two. The composition of the insoluble compound obtained at 20° C therefore differs from the compound obtained at 100° C, the composition of which is $Pd(\alpha\beta)_2$. Although the third $\alpha\beta$-molecule is probably not coordinated to the palladium(II), it is, nevertheless, necessary for the formation of the *insoluble* compound.

CONCLUSIONS AND ANALYTICAL ASPECT

Apart from copper, palladium(II) can be determined in the presence of $\geqslant$99.5% of all other metals tested. The determination can be carried out safely in 50% alcoholic-mineral acid solution in the presence of bi- or trivalent metals. 0.2-0.5 mg of palladium in 20 ml solution are necessary and the error is mostly less than 2%. In the presence of uncoloured cations a red filter must be used, but in the presence of most of the coloured cations (Ni^{+2}, Fe^{+3}, Cr^{+3}) no filter should be used. In the presence of cobalt a blue filter is used in place of the red. In the presence of ferric iron, excesses of tartaric acid must be added.

The foreign metals, if present in large excesses, must be present as nitrates. If chlorides are present in large amounts either no precipitation occurs at all or the density values are very considerably reduced and no maximum point is obtained.

The end-point of the titration is always obtained at the molar ratio of 1 Pd : 3 $\alpha\beta$.

General procedure

20 ml of the analysed solution should contain: 0.2-0.5 mg of palladium (II) as chloride or nitrate, about 1 ml *M* nitric acid and 10 ml alcohol. The solution is titrated with a $\sim$ 0.005*M* α-nitroso-β-naphthol (dissolved in alcohol) The titration time is approximately 20-25 minutes and the error is less than 2%. In the presence of excesses of foreign salts they should be present as nitrates.

a. *Titrations in the absence of foreign metals or in the presence of excesses of uncoloured cations.*
The composition is the same as before. A red filter must be used in all cases.

b. *Titrations in the presence of excesses of coloured cations.*
The composition remains the same as before. In the presence of excesses of chromium(III) or nickel, no filter should be used. In the presence of excesses of cobalt, a blue filter should be used. In the presence of nickel, half the amount of palladium is sufficient for the analysis.

c. *Titrations in the presence of iron(III).*
The above standard solution should contain, in addition, tartaric acid in a molar amount twice as great as the molar amount of iron. No filter should be used. Half the amount of palladium is sufficient for the determination.

SUMMARY

0.2-0.5 mg palladium in 20 ml acid solution may be determined heterometrically, without previous separation, with α-nitroso-β-naphthol. The following foreign metals were present and made up $\geqslant$ 99.5% of the total: Ca, Ba, Mg, Zn, Mn, Ni, Co, Al, Cr, Fe, Pb, Cd and Hg. The error was generally less than 2%.

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RÉSUMÉ

0.2 à 0.5 mg de palladium, dans 20 ml de solution acide, peuvent être dosés par la méthode hétérométrique, au moyen de l'α-nitroso-β-naphtol, sans séparation préalable. Les essais ont été effectués en présence des éléments suivants: Ca, Ba, Mg, Zn, Mn, Ni, Co, Al, Cr, Fe, Pb, Cd et Hg. Ces éléments, en quantités égales ou supérieures à 99.5% ne gênent pas. L'erreur est généralement inférieure à 2%.

ZUSAMMENFASSUNG

0.2-0.5 mg Palladium in 20 ml saurer Lösung kann heterometrisch, ohne vorherige Trennung mit α-Nitroso-β-naphtol bestimmt werden. Die anwesenden Fremdmetalle machten $\geqslant$ 99.5% aus; es waren: Ca, Ba, Mg, Zn, Mn, Ni, Co, Al, Cr, Fe, Pb, Cd und Hg. Der Fehler war meistens kleiner als 2%.

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A NEW METHOD FOR THE BROMATOMETRIC DETERMINATION OF ANTIMONY IN LEAD- AND TIN BASE ALLOYS

by

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INTRODUCTION

Most methods for the volumetric determination of antimony in lead- and tin base alloys are based on decomposition of the alloy by heating with concentrated sulfuric acid, followed by titration of Sb^{+3} with bromate or permanganate after addition of diluted hydrochloric acid. In testing these methods, we experienced irregular difficulties with the decomposition of white metals; the lead sulfate incidentally did not become white, or only after prolonged heating; and results obtained by analysts differed by many per cent.

Difficulties with the decomposition of lead-antimony alloys by these methods are reported by SHAW, WHITTEMORE AND WESTBY[1] and WOOTEN AND LUKE[2]. Moreover, lead sulfate adsorbs Sb^{+3}.

One way to avoid these difficulties is the well-known decomposition of the alloy by hydrochloric acid and bromine or potassium chlorate.

It is a great advantage that the method is of general application and that a clear solution is obtained, though dissolution by this method may last many hours. The possibility of dissolving the alloy by hydrobromic acid and bromine, as proposed by DELASSUS[3] seems promising; even *ca.* 1 g of rather pure lead dissolves completely in less than an hour.

Oxidimetric methods for the determination of antimony have the advantage that the standard solutions are easy to prepare and stable; one of the most accurate methods is, after the opinion of many authors, the titration of Sb^{+3} with bromate. The determination of the end-point with an indicator, *e.g.* methyl orange, has the disadvantage of premature destruction of the indicator by a local excess of bromine; potentiometric determination of the end-point is therefore preferred.

Because decomposition of the alloy with hydrochloric acid and bromine or potassium chlorate gives Sb^{+5}, whereas bromatometric titration of Sb^{+3} is chosen, Sb^{+5} has to be reduced to Sb^{+3}.

A potentiometer may give a check on the quantitative reduction of Sb^{+5}, as well as an ideal control on any excess of reductant. The reduction of Sb^{+5} can be achieved in many ways. NISSENSON AND SIEDLER[4], SHAW, WHITTEMORE AND WESTBY[1] and ANDERSON[5] carry out the reduction with sodium sulfite, JANDER AND BRÜLL[6] with potassium pyrosulfite. HOWDEN[7] uses stannochloride. PŘIBIL AND CHLEBOVSKÝ[8] and

CHLEBOVSKÝ AND BRHÁCEK[9] reduce Sb^{+5} with chromous chloride. ZINTL AND WATTENBERG[10] reduce Sb^{+5} in hot hydrochloric acid solution by adding Ti^{+3}-chloride solution, until the potential of a platinum electrode has dropped below a certain value. As^{+5} is, according to these authors, only very slowly reduced under these circumstances. The reductant can very easily be prepared by dilution of a commercially available solution; moreover, the method will be free of interference by arsenic, without the need of elimination, *e.g.* by destillation.

THEORETICAL PART

The approximate potentials of some interesting redox couples in 1-10*N* hydrochloric acid are plotted in Fig. 1. If the alloy, *e.g.* a white metal, has been dissolved in hydrochloric acid-bromine mixture, the solution may contain (see Fig. 1): Br_2 and Br^- (II), Sb^{+5} (IV), Fe^{+3} (V), As^{+5} (VI), Cu^{+2} (VII), Sn^{+4} (X), Bi^{+3} (XII) Pb^{+2}, Zn^{+2}.

After boiling off the excess bromine and adding Ti^{+3} solution till the potential of a platinum electrode has dropped to *ca.* —50 mV (*vs.* s.c.e.), the solution may contain (see Fig. 1): Br^- (II), Sb^{+3} (IV), Fe^{+2} (V), As^{+5} (VI), Cu^+ (VII), Sn^{+4} (X), Ti^{+4} and Ti^{+3} (XI), Bi^{+3} (XII), Pb^{+2}, Zn^{+2}. From Fig. 1 can be seen, that the potentiometric titration of Sb^{+3} (IV) may meet interference from Fe^{+2} (V) and Cu^+ (VII). Some lead- or tin base alloys contain rather much copper; iron occurs in general only in traces. The titration of Sb^{+3} in the presence of Cu^+ is therefore most important.

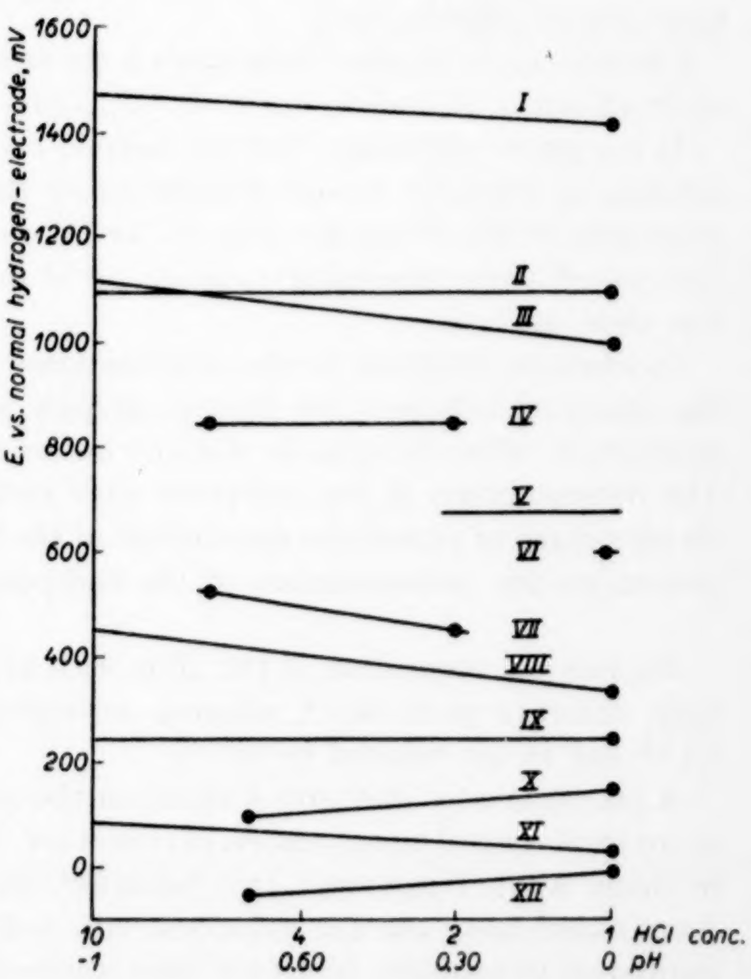

Fig. 1. Approximate potentials (25°) of the redox couples BrO_3^- — Br^- (I); Br_2 — Br^- (II); V^{+5} — V^{+4} (III); Sb^{+5} — Sb^{+3} (IV); Fe^{+3} — Fe^{+2} (V); As^{+5} — As^{+3} (VI); Cu^{+2} — Cu^+ (VII); V^{+4} — V^{+3} (VIII); Sn^{+4} — Sn^{+2} (X); Ti^{+4} — Ti^{+3} (XI); Bi^{+3} — Bi (XII); potential of the saturated calomel electrode (IX)*.

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* Of the systems BrO_3^- — Br^- (I); Br_2 — Br^- (II), V^{+5} — V^{+4} (III), V^{+4} — V^{+3} (VIII) and Ti^{+4} — Ti^{+3} (XI) is, not correct, the redox potential calculated as a function of the pH, supposing that the activity of the H+ions equals the hydrochloric acid concentration. The normal potentials, required for the calculation, are taken from CHARLOT[11].

The values for Sb^{+5} — Sb^{+3} (IV) and Cu^{+2} — Cu^+ (VII) are empirically determined from potentiometric titrations with bromate in 2*N*, resp. 6*N* hydrochloric acid.

The redox potential of Fe^{+3} — Fe^{+2} (V) in 1*N* hydrochloric acid is found in CHARLOT[11], the value in 2*N* hydrochloric acid is determined by potentiometric determination of Fe^{+2} with V^{+5}.

The potentials of Sn^{+4} — Sn^{+2} (X), Bi^{+3} — Bi (XII), As^{+5} — As^{+3} (VI) and the saturated calomel electrode are taken from CHARLOT[11].

Kinetic difficulties in the potentiometric titration of Sb^{+3} with bromate in mixtures of Cu^{+} and Sb^{+3}

It is not impossible, as can be seen from Fig. 1, to titrate potentiometrically Ti^{+3} (XI), Cu^{+} (VII) and Sb^{+3} (IV) with bromate. In fact, the titration curve in 2*N* hydrochloric acid (25°) has a nearly ideal shape (Fig. 2); but the amount of antimony found is much too low, calculating from the bromate consumption between the second and third potential jump. The explanation is a kinetical one, and follows a reasoning given by ZINTL AND WATTENBERG[10]:

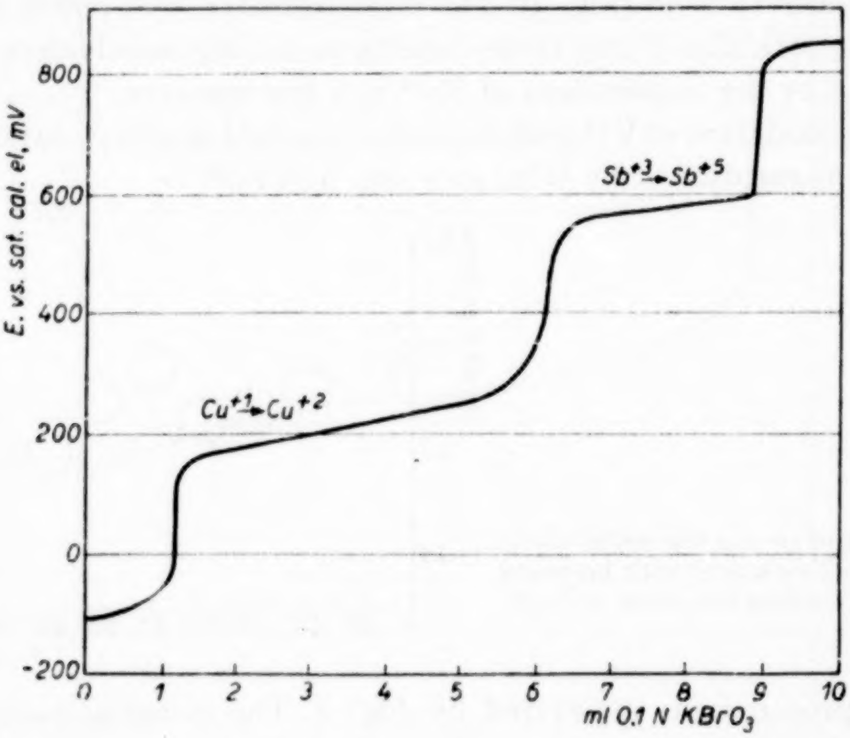

Fig. 2. Titration of a mixture of Cu^{+} and Sb^{+3} in 2*N* hydrochloric acid with bromate at 25°.

> If one tritrates Ti^{+3}, in presence of Cu^{+} and Sb^{+3} with bromate, the titrant will oxidize Cu^{+} with the formation of Cu^{+2} and Sb^{+3} with the formation of Sb^{+5}.
>
> As the reaction $Ti^{+3} + Cu^{+2} \rightarrow Ti^{+4} + Cu^{+}$ is fast, the formation of Cu^{+2} will be temporary as long as Ti^{+3} exists in solution; but, because the reactions $2\,Ti^{+3} + Sb^{+5} \rightarrow 2\,Ti^{+4} + Sb^{+3}$, and $2\,Cu^{+} + Sb^{+5} \rightarrow 2\,Cu^{+2} + Sb^{+3}$ are slow, the prematurely formed Sb^{+5} will not be taken away. The electrode potential is apparently not determined by the redox couple Sb^{+5}-Sb^{+3} as long as one of the other two redox couples is present.

Such a problem could be solved by searching for the thermodynamically *and* kinetically ideal conditions to titrate Sb^{+3} in mixtures with Cu^{+}. This is not a simple matter; at 80°, where reactions are faster, the second potential jump is much less steep than in Fig. 2. It has been found that antimony can be determined by titration of Sb^{+3} with bromate, after oxidation of Ti^{+3} and Cu^{+} with a solution of V^{+5} in hydrochloric acid.

The titration of Sb^{+3} with bromate after oxidation of Ti^{+3} and Cu^{+} with V^{+5}

This procedure is only possible on two conditions:

1) V^{+5} does not, or only slowly, oxidize Sb^{+3};
2) V^{+4} does not reduce bromate, or reduces bromate at a much higher potential than Sb^{+3} does.

Ad 1): Aliquot parts of an Sb^{+3} solution in 2*N* hydrochloric acid were titrated with 0.1*N* potassium bromate after addition of increasing amounts of a 0.1*N* V^{+5} solution in 2*N* hydrochloric acid (Fig. 3). The bromatometric end-points were determined potentiometrically. Under these conditions 0.1 mg aequivalent V^{+5} apparently oxidizes 0.01 mg aequivalent of Sb^{+3} in a few minutes.

Ad 2): The slow oxidation of V^{+4} (sulfate) either in a cold or a hot solution, by potassium bromate is mentioned by WILLARD AND YOUNG[12].

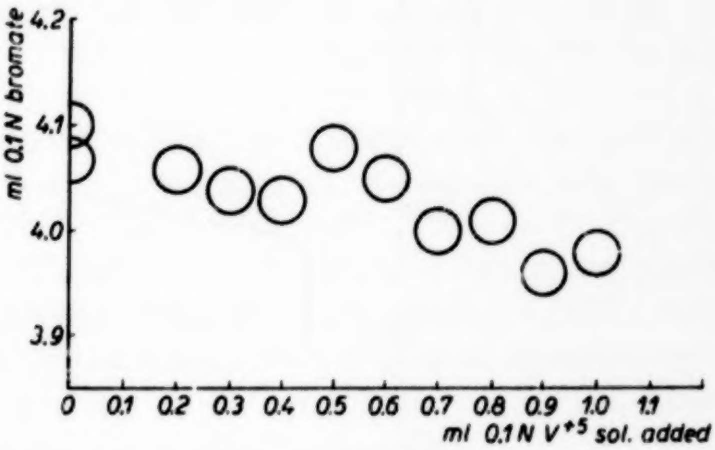

Fig. 3. Titrations of *ca.* 0.4 mg aequivalent Sb^{+3} in 2*N* hydrochloric acid with bromate after adding increasing amounts of 0.1*N* V^{+5} solution.

The adopted procedure is illustrated by Fig. 4. The essential point is, that Sb^{+3} can be titrated with bromate after the potential break at *ca.* 400 mV (*vs.* s.c.e.)

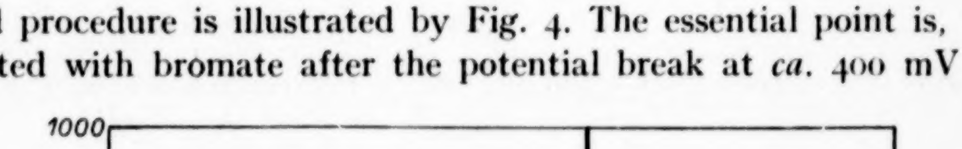

Fig. 4. Potentiometrically checked oxidation of Ti^{+3} and Cu^{+} by V^{+5}, followed by potentiometric titration of Sb^{+3} with potassium bromate.

because of completion of the reaction $Cu^+ + V^{+5} \rightarrow Cu^{+2} + V^{+4}$. The potential break is less pronounced at hydrochloric acid concentrations higher than 3*N* and occurs at a higher potential.

The potential jump at *ca.* 400 mV (*vs.* s.c.e.) is less steep in the presence of iron, because of overlapping of the potential break at *ca.* 400 mV (*vs.* s.c.e.) by the buffering action of the redox couple Fe^{+3} — Fe^{+2}; the reaction $Fe^{+2} + V^{+5} \rightarrow Fe^{+3} + V^{+4}$ is far from completed at 400 mV (*vs.* s.c.e.): see Fig. 1, v and Fig. 5.

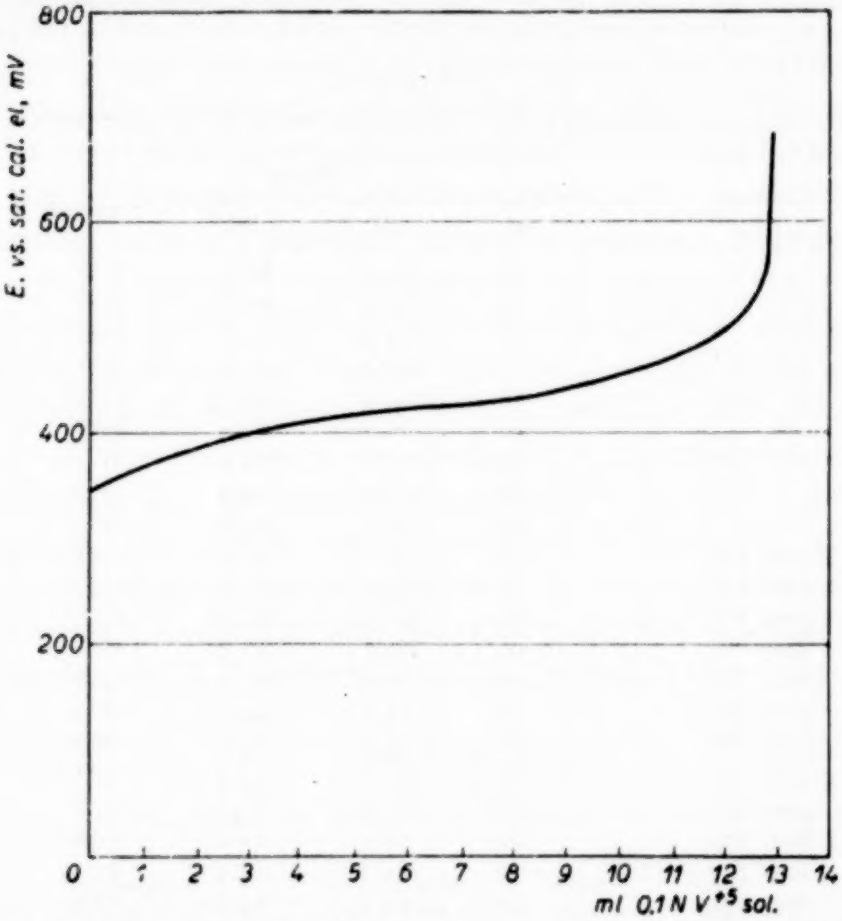

Fig. 5. Titration of 1.3 mg aequivalent of Fe^{+2} in 100 ml 2*N* hydrochloric acid with V^{+5}.

EXPERIMENTAL PART

Tentative procedure

Reagents

Hydrochloric acid — bromine mixture:

Dissolve 10 ml bromine in 100 ml hydrochloric acid (1.19) by shaking.

Potassium bromate 0.1*N*:

Dissolve 2.7835 g potassium bromate *p.a.* (dried at 180°) in 1 l *aqua dest.* The solution can be standardized against arsenic trioxide *p.a.* (dried at 110°) or against pure metallic antimony according to this procedure; 1 ml of this solution titrates *ca.* 6 mg antimony.

V^{+5} 0.1*M*:

Dissolve 4.6 g pure vanadium pentoxide in 40 ml 10% sodium hydroxide. Neutralize with 6*N* hydrochloric acid against litmuspaper, add 300 ml 2*N* hydrochloric acid and dissolve by shaking. Filter if necessary and dilute to 500 ml with 2*N* hydrochloric acid.

Cupric chloride 0.1*M*:

Dissolve 8.5 g cupric chloride ($CuCl_2$.2 *aq.*) in 500 ml 2*N* hydrochloric acid.

Ti^{+3} 0.1*M*:

Dilute 10 ml titanium trichloride solution (15%, iron content less than 0.015%, Merck with 90 ml 2*N* hydrochloric acid. Store in a closed bottle.

Procedure

Dissolve 0.5-1 g alloy by gentle heating in a covered beaker in 25 ml hydrochloric acid-bromine mixture. Add 1.5 ml cupric chloride $0.1\,M$ if the material contains less than 10 mg copper*. More hydrochloric acid-bromine mixture will be required if the lead content of the alloy is high. Remove the excess bromine and some of the excess of hydrochloric acid by boiling down to a volume of less than 20 ml. Dilute with 100 ml $2N$ hydrochloric acid and heat to boiling. Remove from burner or hot plate and add, while stirring (preferably magnetic) Ti^{+3} $0.1\,M$ from a buret to the hot solution while measuring the potential difference between a platinum electrode and a saturated calomel electrode with a tube-voltmeter. (The platinum electrode must be cleaned before each determination by immersion in warm nitric acid (1.4) during a few seconds.)

Stop the addition of Ti^{+3} $0.1\,M$ as soon as the potential of the platinum electrode reaches *ca.* —50 mV (*vs.* s.c.e.); the solution should be faintly violet. Cool to room temperature, preferably

TABLE I

DETERMINATION OF ANTIMONY BY TITRATION WITH $0.1\,N$ POTASSIUM BROMATE

Serial nr.	*Element mg*	*Copper mg*	*Antimony taken mg*	*Antimony found mg*	*Analyst*	△ *Sb mg*	△ *Sb % rel.*
1		20	60.2	60.1	vdV	—0.1	—0.2
2		20	60.2	60.0	vdV	—0.2	—0.3
3		20	24.1	24.1	vdV	0.0	0.0
4		—	60.2	60.0	vdV	—0.2	—0.3
5		50	60.2	59.8	vdV	—0.4	—0.7
6		50	60.2	60.4	Win	+0.2	+0.3
7		50	24.1	24.2	Win	+0.1	+0.4
8		50	24.1	24.0	Win	—0.1	—0.4
9		50	60.2	59.8	Win	—0.4	—0.7
10	400 Pb	20	24.1	23.9	vdV	—0.2	—0.8
11	400 Pb	20	24.1	24.2	vdV	+0.1	+0.4
12	400 Pb	20	60.2	60.1	vdV	—0.1	—0.2
13	400 Pb	20	60.2	60.3	vdV	+0.1	+0.2
14	800 Pb	20	24.1	24.2	vdV	+0.1	+0.4
15	800 Pb	20	24.1	24.2	Win	+0.1	+0.4
16	800 Pb	20	24.1	24.3	Win	+0.2	+0.8
17	400 Sn	20	24.1	24.4	vdV	+0.3	+1.2
18	400 Sn	20	60.2	60.2	vdV	0.0	0.0
19	800 Sn	20	24.1	23.9	vdV	—0.2	—0.8
20	800 Sn	100	24.1	24.1	Win	0.0	0.0
21	800 Sn	20	24.1	24.2	Win	+0.1	+0.4
22	400Pb+400Sn	20	24.1	24.2	Win	+0.1	+0.4
23	400Pb+400Sn	100	60.2	60.3	Win	+0.1	+0.2
24	400Pb+400Sn	20	24.1	24.3	Win	+0.2	+0.8
25	400Pb+400Sn	20	60.2	60.4	Win	+0.2	+0.3
26	0.5 Fe	20	60.2	60.1	vdV	—0.1	—0.2
27	1.0 Fe	20	60.2	60.5	vdV	+0.3	+0.5
28	1.5 Fe	20	60.2	60.4	vdV	+0.2	+0.3
29	3.0 Fe	20	60.2	60.1	vdV	—0.1	—0.2
30	5 Bi	20	48.2	48.2	vdV	0.0	0.0
31	5 Bi	20	48.2	48.3	vdV	+0.1	+0.2
32	60 As	20	0	0.1	vdV	+0.1	
			% Sb according certificate	*% Sb found*			
33			12.04	12.00	vdV	—0.2	—0.3
34	BCS 177		12.04	11.97	vdV	—0.4	—0.6
35	(lead base)		12.04	11.98	vdV	—0.3	—0.5
36			12.04	11.99	vdV	—0.2	—0.4
37	BCS 178		7.51	7.38	vdV	—1.0	—1.8
38	(tin base)		7.51	7.36	vdV	—1.2	—2.0
39			7.51	7.39	vdV	—0.9	—1.6
40			7.51	7.39	vdV	—0.9	—1.6

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* The end-point of the reaction $Cu^{+} + V^{+5} \rightarrow Cu^{+2} + V^{+4}$ serves to indicate completion of the oxidation of all cations, except Sb^{+3}, to their highest valency.

by filling the space between the titration beaker and a wider concentric beaker, with ice. The potential of the platinum electrode may rise to *ca.* + 100 mV while cooling because of air oxidation of Ti^{+3}, catalysed by the redox couple Cu^{+2} — Cu^{+}. V^{+5} 0.1*M* is then delivered dropwise from a buret, till one drop causes a potential jump of 50-100 mV at *ca.* 400 mV (*vs.* s.c.e.); in case of doubt, another drop of V^{+5} 0.1*M* may be added. After the potential jump, the E.M.F. increases very slowly in the time till *ca.* 500 mV. If more than 1 mg of iron is present, add V^{+5} 0.1*M* till the potential of the platinum electrode is 500 mV (*vs.* s.c.e.). Titrate with potassium bromate 0.1 *N* until the potential increases sharply because of the appearance of free bromine. Calculate the amount of antimony from the bromate consumption.

Checking of the tentative procedure

The tentative procedure has been tested on synthetical mixtures and British Chemical Standards. The results are summarized in Table I. The accuracy of the test is limited by the fact that the titrations were carried out with potassium bromate 0.1*N* (1 ml = 6 mg antimony), delivered from an ordinary 50 ml buret; the results with the synthetic mixtures are therefore judged satisfactory in presence of 800 mg lead, 800 mg tin, 100 mg copper, 5 mg bismuth, 60 mg arsenic, 1 mg iron. The percentage of antimony found in the British Chemical Standards — especially in the tin base alloy — is less than the certificates (d.d. 1925, resp. 1930) give.

A more sensitive check of the method consists of titrating with potassium bromate 0.02*N*. The titer of this solution is determined by potentiometric determination against arsenic trioxide *p.a.* or against pure metallic antimony according to the foregoing prescription. The results are summarized in Table II. At nr. 53, 10 ml H_3PO_4 (85%) was added before oxidizing with V^{+5}; however, the end-point of the oxidation by V^{+5} was not marked by the potential jump which occurs in the absence of iron and phosphoric acid. V^{+5} was added till the potential was +500 mV (*vs.* s.c.e.).

TABLE II

DETERMINATION OF ANTIMONY BY TITRATION WITH 0.02*N* POTASSIUM BROMATE

Serial nr.	*Element mg*	*Copper mg*	*Antimony* *taken mg*	*Antimony* *found mg*	△ *Sb* *mg*	△ *Sb* *% rel.*
41		20	9.97	9.94	−0.03	−0.3
42		20	0.00	0.05	+0.05	
43		10	39.88	39.76	−0.12	−0.3
44	20 As, 20 Bi	10	10.01	10.07	+0.06	+0.6
45	10 Ni, 10 Zn, 10 Al	10	19.94	19.89	−0.05	−0.3
46	1 Fe	10	20.02	20.06	+0.04	+0.2
47	10 Fe	10	20.02	20.43	+0.41	+2.0
48	400 Pb, 400 Sn	20	10.01	10.06	+0.05	+0.5
49	400 Pb, 400 Sn	20	0.00	0.09	+0.09	
50	400 Pb, 400 Sn	10	40.05	40.20	+0.15	+0.4
51	400 Pb, 400 Sn, 10 Ni, 10 Zn, 10 Al	10	20.02	20.02	0.00	0.0
52	1 Fe, 400 Pb, 400 Sn	10	20.02	20.04	+0.02	+0.1
53	10 Fe, 400 Pb, 400 Sn (10 ml 85% phosphoric acid added after reduction with Ti^{+3})	10	20.02	20.09	+0.07	+0.3

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SUMMARY

Kinetic difficulties in the potentiometric bromatometric determination of Sb^{+3} in presence of Cu^{+} etc., can be solved by oxidizing bromate-reducing ions save Sb^{+3} with V^{+5} before titrating Sb^{+3} with bromate: V^{+5} reacts very slowly with Sb^{+3} and potassium bromate is very slowly reduced by V^{+4}. Much iron interferes. A method for the determination of antimony in lead- and tin base alloys is given and tested.

RÉSUMÉ

Les auteurs démontrent que les difficultés cinétiques, lors du dosage potentiométrique de Sb^{+3} par le bromate, en présence de Cu^{+} etc., sont éliminées, si l'on oxyde, au préalable, tous les ions réduisant le bromate (mais pas l'antimoine) par le V^{+5}, V^{+5} ne réagissant que très lentement avec Sb^{+3}, et V^{+4} ne réagissant que très lentement avec le bromate. De grandes quantités de fer gènent le dosage. Un mode opératoire pour le dosage de l'antimoine dans ses alliages à base de plomb-étain est décrit.

ZUSAMMENFASSUNG

Kinetische Schwierigkeiten bei der potentiometrischen Titration von Sb^{+3} mit Bromat in Gegenwart von Cu^{+} usw., können dadurch gelöst werden, dass man vor der Titration von Sb^{+3} mit Bromat die anderen bromatreduzierenden Ionen mit V^{+5} oxydiert; V^{+5} reagiert nur sehr langsam mit Sb^{+3}, und V^{+4} reagiert sehr langsam mit Bromat. Grössere Mengen Eisen stören die Bestimmung. Ein Verfahren für die Bestimmung von Antimon in Blei-Zinn Legierungen wird gegeben.

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POTENTIOMETRIC DETERMINATION OF FRACTIONAL MILLIGRAM-QUANTITIES OF URANIUM IN ZIRCONIUM

by

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Several methods are available for the colorimetric determination of fractional milligram-quantities of uranium[1,2,3] but difficulty is encountered when zirconium is present in appreciable amounts. For this reason, a rapid volumetric method was sought.

COOKE *et al.*[4] and SILL AND PETERSON[5] proved the effectiveness of the lead reductor, showing that uranium(VI) is rapidly and completely reduced to uranium (IV). The uranous solution is subsequently titrated with dichromate[1,4,6,7], permanganate[1,6,8,9], ferric[1,9], or ceric[1,8,10,11] solutions. The SILL AND PETERSON titration is inapplicable without prior separation of the zirconium, since the phosphoric acid catalyst precipitates zirconium, and interferes with the end-point of the titration.

The facile hydrolysis of zirconium salts necessitates a solution of relatively high acidity (3*N* in hydrochloric acid) and sulfatoceric acid is a stable titrant at this acidity.

The object of this study was to investigate the titration of uranium without prior separation of the zirconium. The method has application in the analyses of sheet zirconium and zirconium-uranium alloys which are used in nuclear energy reactors.

PROCEDURE

Preparation of the sample

Solution of metal. Weigh the sample into a platinum crucible and add 5 ml of concentrated perchloric acid. Add hydrofluoric acid dropwise, with heating, until the sample completely dissolves. Fume to a small volume. Cool.

Titration of the sample

Transfer the sample to a 50-ml beaker (marked at 20-ml) with water. Add 5 ml of concentrated hydrochloric acid and dilute to the 20-ml volume mark with water. Pass the sample through the lead reductor and catch the eluant in a 100-ml beaker containing 5 ml of concentrated hydrochloric acid and 2 ml of ferric ammonium sulfate solution (20% solution in 5% sulfuric acid). Wash the first beaker and the reductor several times with a total of 20 ml of 10% hydrochloric acid and catch the washings in the beaker containing the reduced iron solution. Titrate potentiometrically (platinum-calomel electrode system) with standard sulfatoceric acid of suitable concentration. A magnetic stirrer is useful for mixing the sample during the titration. The end-point occurs between 600 and 800 millivolts. Prepare a reductor-indicator blank, following the sample procedure, but omit the sample.

The sulfatoceric acid solution was standardized against sodium oxalate according to the directions of SMITH[12].

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APPARATUS

Lead reductor

The reductor column was made from 10-mm glass tubing, and was packed to a height of 31 cm with lead. The reductor was otherwise prepared according to the reference cited[5].

EXPERIMENTAL RESULTS AND DISCUSSION

In the preliminary runs only uranium (10 to 0.1 mg) was studied. Potentiometric readings were taken simultaneously with the visual titration readings by the SILL AND PETERSON method. Platinum-calomel electrodes were used. The electrolyte contained phosphoric acid in 2N hydrochloric acid solution, the indicator was ferroin and the titrant was 0.01N sulfatoceric acid. The potentiometric end-point is near the visual end-point (ferroin), but the potentiometric indicator is not usable (under these conditions) when the uranium content is less than 1 mg. By reducing the volume one-half, as little as 0.1 mg of uranium may be detected, but the millivolt-change at the end-point was rather slow.

The next series of experiments was pointed toward improving the potentiometric end-point in the presence of uranium alone. The acidity was increased from 2N hydrochloric acid to 3 to 4N[4,10] and the reduced uranium solution was treated with ferric ammonium sulfate[1,7] to produce ferrous ion. The latter was to be determined potentiometrically. The effect of ferric ion concentration, as well as increases in hydrochloric acid content, were ascertained. The total volume of solution was then reduced to an operational minimum and the concentration of uranium in the test samples reduced, step wise, to the point where the potentiometric break was too small for practical use.

A titration blank can be set up to absorb reproducible errors such as reducing materials in the ferric-ion solution, materials in the hydrochloric acid solution which are reduced by passage through the lead column, and the ionic or mass effects of the ferric ion solution. The correction for the blank is reasonably small. Table I shows the blank correction would be approximately 0.3 ml of 0.001N sulfatoceric acid solution; this correction volume is equivalent to 0.03 mg of uranium.

Table I also shows the effect of higher concentrations of ferric-ion solution on the blank. The concentration of ferric ion present is not critical, but quantities over 50 mg per 50 ml tend to decrease the potentiometric break. This effect was also noted when the concentration of ferric ion was varied in the presence of uranium. For this reason the optimum concentration of ferric ion appears to be 10 to 50 mg (or 0.5 to 2 ml of the 20% ferric ammonium sulfate solution).

TABLE I

EFFECT OF CONCENTRATION OF FERRIC ION ON BLANK

Fe^{+3} mg	0.001N Ce^{+4} ml	Potentiometric break mV
0	0.25, 0.35	100
11	0.25, 0.35	130, 190
46	0.25, 0.55	110, 150
115	0.55	50
230	0.45	35

Table II shows data in the range from 5 to 0.1 mg of uranium. The potentiometric breaks are satisfactory throughout the test runs; with one exception, the breaks are about 100 millivolts or more. The "range" and "standard deviation" are calculated, using DEAN AND DIXON's [13] shortcut method. The results in Table II demonstrate the applicability of this potentiometric procedure for the determination of as little as 0.1 mg of uranium in aqueous solution. This is the basis for the final series of tests with zirconium present.

TABLE II

POTENTIOMETRIC TITRATION OF URANIUM

3 to 4*N* HCl-ferric solution

Taken U	*Found*			*Potentiometric break*	*Statistics*
mg	*0.01N Ce^{+4} ml*	*0.001N Ce^{+4} ml*	*U mg*	*mV*	
5.35	4.43		5.32	160	
	4.45		5.35	200	
	4.45		5.35	190	
	4.45		5.35	180	w = 0.03
					S_w = 0.01
1.07		8.71	1.04		
		8.75	1.04	100	
	0.88		1.07	220	
	0.88		1.07	100	
	0.88		1.07	200	
					w = 0.03
					S_w = 0.01
0.54		4.32	0.51	110	
	0.45		0.55	85	
0.32		2.55	0.30	80	
		2.89	0.34	110	
0.21		1.82	0.22	100	
		1.83	0.22	50	
		1.87	0.22	90	
		1.90	0.23	120	
					w = 0.01
					S_w = 0.005
0.11		0.83	0.10	100	
		0.85	0.10	100	
		0.90	0.11	100	
		0.98	0.12	100	
	0.10		0.12	120	
					w = 0.02
					S_w = 0.01

Zirconium (as the chloride or sulfate) was introduced to determine the effects on the titration. (Insoluble zirconyl phosphate was formed when the SILL AND PETERSON method was followed and interference was noted.) The zirconium solution was passed through the reductor and treated with ferric-ion solution. The subsequent potentiometric curves were examined for variations in blanks and in end-points, and the presence of zirconium did not produce any undesirable effects. Following this, a series of zirconium-uranium test solutions were run, and in this manner, the limiting ratio of concentrations of uranium to zirconium was established. Particular interest was directed toward the determination of 0.1% uranium in zirconium when the amount of uranium present was 0.1 mg. The results in Table III show this can be accomplished. The "range" and "standard deviation" were calculated by DEAN AND DIXON's[13] method and are in range of the 3 S_w spread as recommended by LIEBHAFSKY[14].

TABLE III

DETERMINATION OF URANIUM IN SYNTHETIC SOLUTIONS IN THE PRESENCE OF ZIRCONIUM POTENTIOMETRIC METHOD

Taken			*Found*				*Potentiometric break*	*Statistics*
U mg	*Zr mg*	*% U in Zr*	*0.01N Ce^{+4} ml*	*0.001N Ce^{+4} ml*	*U mg*	*Error mg*	*mV*	
5.35	100	5	4.51		5.42	0.07	100	
5.35	300	2	4.46		5.36	0.01	80	
1.07	50	2	0.88		1.07	0.0	120	
1.07	100	1	0.88		1.07	0.0	150	
1.07	100	1		8.95	1.07	0.0	40	
1.07	300	0.4	0.96		1.16	0.09	130	
1.07	300	0.4	0.92		1.12	0.05	80	
1.07	500	0.2	0.94		1.14	0.07	55	
1.07	500	0.2	0.94		1.14	0.07	80	
1.07	500	0.2		8.72	1.04	0.03	30	
								w = 0.12 S_w = 0.04
0.54	100	0.5		4.91	0.58	0.04	80	
0.54	100	0.5		5.00	0.50	0.04	50	
0.54	400	0.1		4.60	0.55	0.01	20	
0.54	500	0.1		4.05	0.48	0.06	20	
								w = 0.10 S_w = 0.05
0.21	50	0.4		1.90	0.23	0.02	90	
0.21	100	0.2		2.00	0.24	0.03	65	
0.21	100	0.2		1.93	0.23	0.02	85	
0.21	100	0.2		1.90	0.23	0.02	75	
0.21	200	0.1		2.10	0.25	0.04	40	
0.21	200	0.1		2.00	0.24	0.03	40	
0.21	500	0.04		2.10	0.25	0.04	30	
								w = 0.02 S_w = 0.01
0.11	50	0.2	0.10		0.12	0.01	75	
0.11	100	0.1	0.12		0.14	0.03	90	
0.11	100	0.1		0.95	0.11	0.00	80	
0.11	200	0.05		1.00	0.12	0.01	60	
								w = 0.03 S_w = 0.01

Table IV compares the potentiometric method with other routine methods for uranium determination. The gravimetric (pyridine) method[15] and the perchloric acid colorimetric method[16] are useful for the "higher" uranium contents, while the 8-quinolinol[3] and thiocyanate-pentaether methods[2] may be extended below the lowest sensitivity of the potentiometric method. On the other hand, if zirconium is present the gravimetric method is not applicable; the perchloric acid colorimetric method is useful in the presence of zirconium only if the uranium content is at least 10 mg. The thiocyanate-pentaether colorimetric method may be used to determine microgram-quantities of uranium, only if the zirconium content is less than 50 mg, and the 8-quinolinol method is not satisfactory in the presence of milligram-quantities of zirconium.

TABLE IV

COMPARISON OF CASUAL[a] URANIUM SAMPLES BY SEVERAL METHODS

Sample	*Potentiometric* *mg U*	*Gravimetric Pyridine*[15] *mgU*	*Colorimetric* *$HClO_4$*[16] *mg U*	*KCNS*[2] *mg U*	*8-Quinolinol*[3] *mg U*
A	14.0	13.8	14.0		13.8
	13.9	13.8	14.0		13.8
	13.9	13.7	13.9		
B	1.10			1.02	
	1.07			0.98	
	1.07			1.00	
	1.07			1.00	
C	4.61				4.41
D	0.38				0.37
E	0.07				0.06

[a] Composition of samples unknown.

In the past, it was frequently recommended that iron and zirconium be removed by a preliminary cupferron separation[17], but SILVERMAN, MOUDY AND HAWLEY[3] found small amounts of uranium in the cupferrate extracts and precipitates. Double cupferron separations and double fumings with perchloric acid are required to recover all the uranium. In such cases where the iron content is small, it is preferable to determine the small amount of iron colorimetrically, and to subtract its equivalent uranium value from the apparent uranium result.

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SUMMARY

Optimum conditions have been established for the potentiometric titration of uranium in the presence of zirconium. The uranyl chloride solution is passed through a lead reductor, the eluant is caught in a ferric iron (phosphate-free) solution, and is titrated with sulfatoceric acid solution. The titration is conducted in a 3*N* hydrochloric acid solution and the presence of the ferric solution (of limited concentration) increases the millivolt-change at the end-point. The lower limit for the determination of uranium is 0.1 mg, and in the presence of zirconium, the minimum weight ratio is 1 to 1,000.

RÉSUMÉ

Les conditions optima ont été établies pour le titrage potentiométrique de l'uranium en présence de zirconium. On fait passer la solution de chlorure d'uranyle à travers un réducteur au plomb, l'éluant est reçu dans une solution de fer(III) (exempte de phosphate) et titré par une solution d'acide sulfatocérique. Le titrage est effectué en solution d'acide chlorhydrique 3*N*; la présence de fer(III) (de concentration limitée) augmente le saut au point final La limite inférieure pour le dosage de l'uranium est de 0.1 mg; en présence de zirconium, le rapport minimum des poids doit être 1 : 1,000.

ZUSAMMENFASSUNG

Die besten Bedingungen für die potentiometrische Titration von Uran in Gegenwart von Zirkonium wurden ermittelt. Die Uranylchloridlösung wird durch einen Bleireduktor geführt und die erhaltene Lösung in einer phosphatfreien Eisen(III)-Lösung aufgefangen und mit saurer Cersulphatlösung titriert. Die Titration wird in 3*N* Salzsäure ausgeführt; durch die Gegenwart der Eisen(III)-Lösung wird der Sprung am Endpunkt erhöht. Die untere Grenze für die Uranbestimmung beträgt 0.1 mg, während in Gegenwart von Zirkonium das minimale Gewichtsverhältnis 1 : 1,000 ist.

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CONDUCTOMETRIC TITRATIONS OF ORGANIC BASES WITH BORON TRIBROMIDE IN APROTIC SOLVENTS

by

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INTRODUCTION

The literature contains a number of references[1-5] to the titration of Lewis acids and bases in non-aqueous solvents. MANDELL[6] has reported a reaction between boron tribromide and nitrobenzene. Little use has been made of boron tribromide as an acid in non-aqueous solvents. In the present work, conductance titrations have been carried out to determine the nature of the reaction of boron tribromide with organic bases. Several anhydrous aprotic solvents were selected as reaction media.

EXPERIMENTAL

Materials

Thionyl chloride was distilled in an all glass still as described by LUDER[4,5]. Pyridine, quinoline and isoquinoline were dried over sodium hydroxide pellets and distilled through a Vegreux column collecting only a small central portion. The products were stored in a dispensing flask with a sodium hydroxide magnesium perchlorate drying tube. Nitrobenzene was stored over sodium carbonate and treated in a similar manner. Thiophosphoryl chloride (Westvaco Chemical Division — Food Machinery and Chemical Corp.) was used as received after drying and storing in a dispensing flask. Boron tribromide was prepared by a modification of a procedure suggested by GAMBLE *et al.*[7].

The boron tribromide was distilled twice and the colorless liquid stored in a special dispensing burette with a drying tube and Teflon stopcock.

Other reagents were stored in specifically designed florence flasks with side arm burettes joined to the side. A drying tube was stoppered into the neck of the flask. Delivery of the reagent was accomplished through a Teflon stopcock thus avoiding any errors due to stopcock grease or other contaminents.

Procedure

A standard type conductance cell[8] was employed which had about a 40 ml capacity. Platinum electrodes were placed in side arms imbeded in the side of the cell in the conventional manner. A third side arm was fused to the conductance cell for the purpose of passing dry nitrogen over the solution during the titration. The conductance measurements were carried out in a constant temperature bath accurate to 250° C ± 0.05. Nitrogen dried by successive passage through Drierite, magnesium perchlorate and phosphorous pentoxide was passed over the surface of the reactants. A plastic cover was fitted over the cell. A burette tip was inserted through a hole in the cover. The titrant was added in known amounts directly to the cell and conductance measured at five minute intervals by means of a Surfass conductivity bridge.

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[*] Based upon a thesis submitted by MALCOLM C. HENRY to the Faculty of the University of Pennsylvania in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

RESULTS

Fig. 1 shows the reaction between pyridine and quinoline with boron tribromide using nitrobenzene as a solvent. In this case the organic base was added to a solution of boron tribromide in nitrobenzene. The reaction between the solvent and boron tribromide was found to yield a 1:1 addition compound which is highly dissociated and soluble in excess nitrobenzene. On addition of quinoline or pyridine the stronger base displaced the weaker base, nitrobenzene, from its complex with boron tribromide. The initial conductance arose from the dissociation of the addition compound formed in the interaction between the boron tribromide and the nitrobenzene. The dissociation of the addition compound may be visualized in the following reaction:

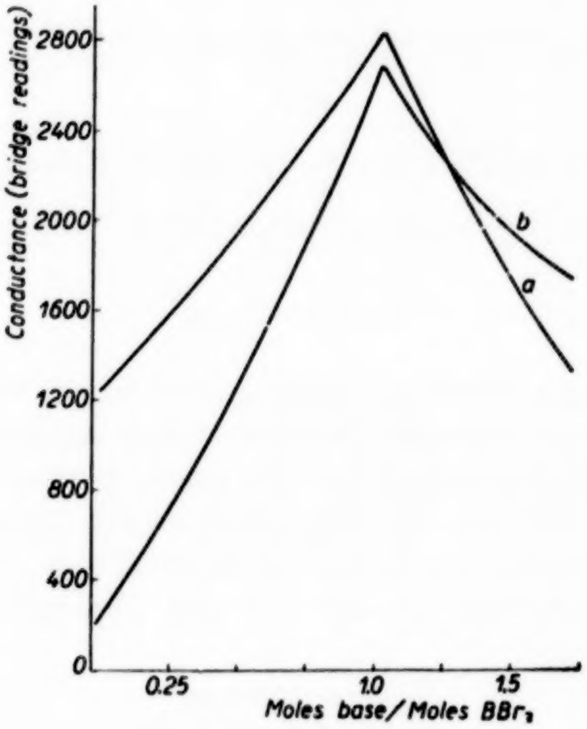
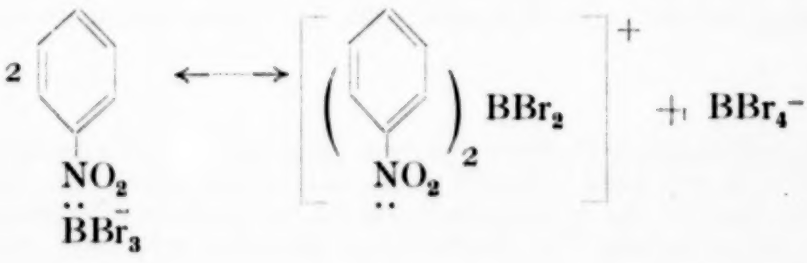


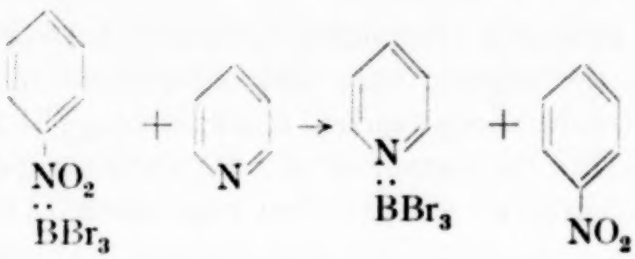
Fig. 1. Nitrobenzene
a) Pyridine, b) Quinoline



Addition of pyridine (curve a) and quinoline (curve b) changed the reaction so that the favored reaction was between the boron tribromide and the organic base. This formed a more ionogenic compound than the nitrobenzene addition compound as follows:

References p. 192

(1)



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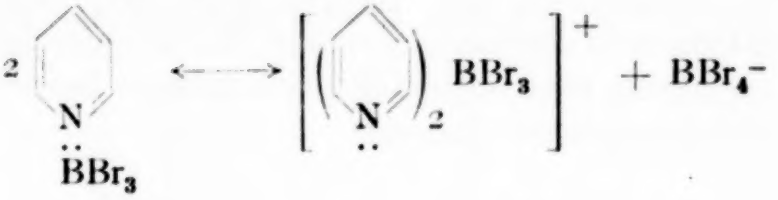


The conductance reached a limiting value corresponding to the formation of a 1:1 complex and then fell off beyond the end-point. This suggests a reversal of process number 2 in excess boron tribromide with a subsequent lessening in ionization. The reduced conductance may be attributed both to the lowering of the dielectric of the system and therefore a decrease of the ionization of the addition compound. Curve 1b shows a larger rate of change of conductance with concentration for the quinoline as compared to that of pyridine. This behavior correlates with the higher base strength of quinoline and possible steric effects introduced by the second ring.

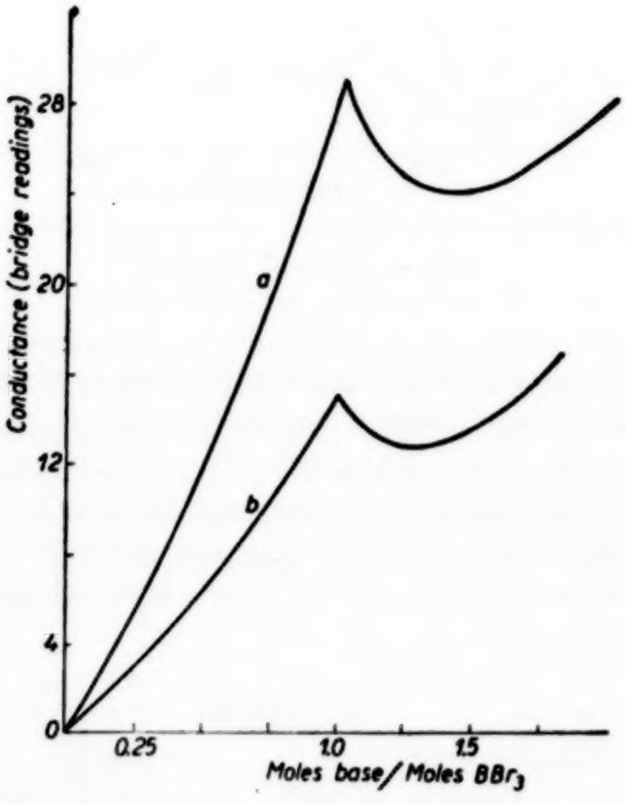


Fig. 2. Thiophosphorylchloride
a) Isoquinoline, b) Quinoline

In Fig. 2 the results of titrating boron tribromide dissolved in thiophosphoryl chloride with isoquinoline and quinoline are noted. The initial zero conductance suggests that there was no reaction between the two acid molecules. The rising portion of the curve indicates compound formation between the strongly acidic boron tribromide and the organic base with subsequent ionization as in Fig. 1. At the end-point the conductance reached a maximum. The reaction was stoichiometric and corresponded to the formation of a 1:1 complex. Beyond the equivalence point the conductance dropped sharply then rose slowly. The rise in conductance beyond the end-point was the result of a slow reaction between the organic base and the solvent. The difference in base strength of the isoquinoline and quinoline is shown by the difference in conductance values. The isoquinoline complex was more highly ionized suggesting that isoquinoline is a stronger Lewis base than quinoline in the solvent thiosphosphoryl chloride.

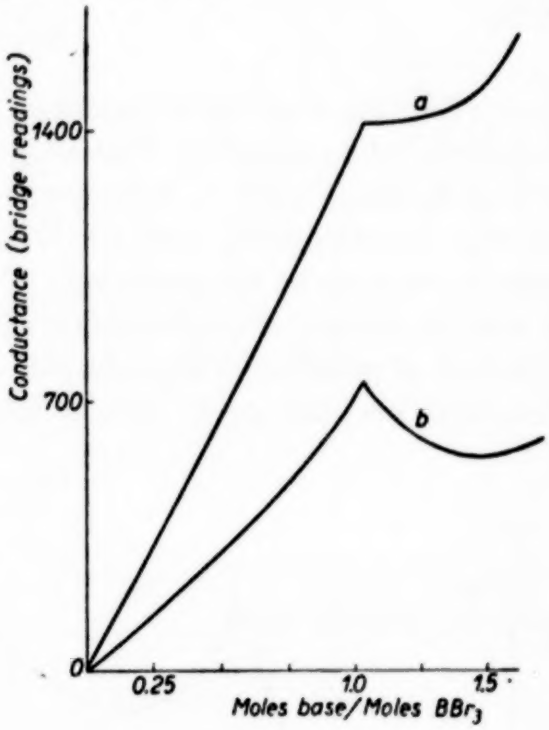
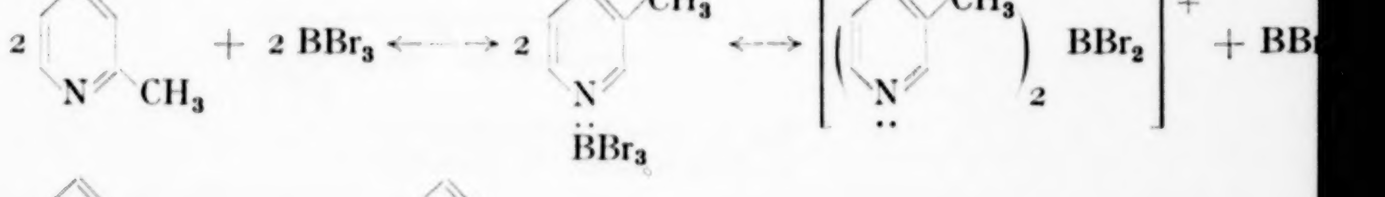


Fig. 3. Thionyl chloride
a) α-Picoline, b) Isoquinoline

Fig. 3 shows the titrations of boron tribromide dissolved in thionyl chloride with the bases, α-picoline and isoquinoline. The preferential reactions were between the bases and the stronger acid, boron tribromide. The completion of these reactions was, in each case, marked by an end-point corresponding to a break in the conductance curve at a 1:1 molecular ratio. Further addition of base resulted in a reaction of the base with the solvent acting as an acid. These successive reactions are illustrated in the following:

(1)


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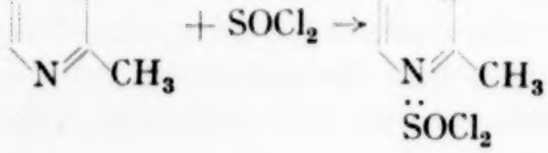

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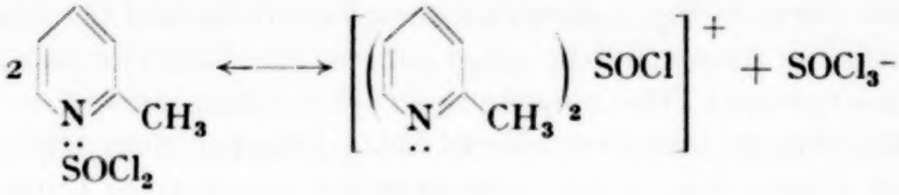
(3)



The reaction of the base with the solvent is seen to be a function of the base strength, the stronger base α-picoline showing a strong reaction with solvent beyond the equivalence point.

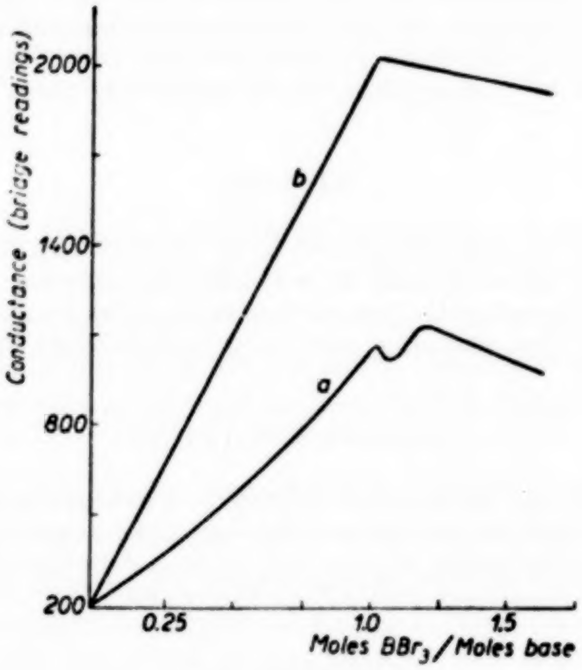
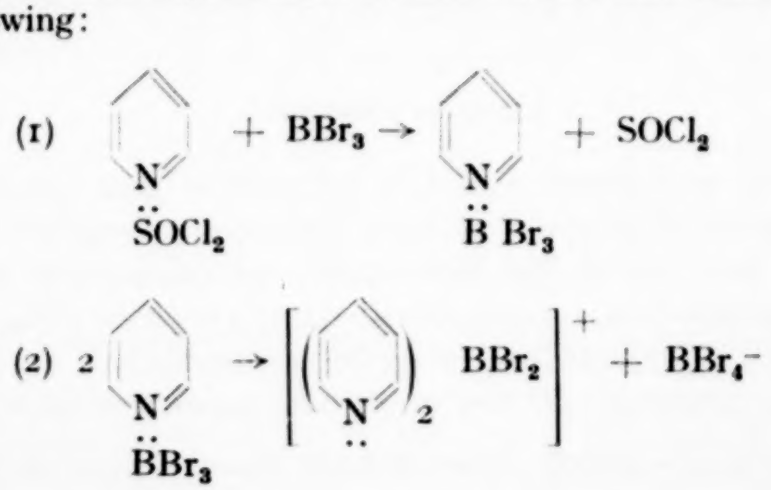


Fig. 4.
a) Pyridine 0.32 M, b) 2-Methyl-5-ethyl-pyridine 0.15 M

Fig. 4 shows the titration of pyridine and 2-methyl-5-ethyl-pyridine with boron tribromide in thionyl chloride. In this case the base was dissolved in the solvent and the boron tribromide used as a titrant. This gave a more uniform and accurate result because the base-solvent reaction was completed before the boron tribromide was added. A similar reaction has been described previously[4]. The addition of boron tribromide resulted in the displacement of the weaker acid from the complex as shown in the following:



The pyridine curve in Fig. 4 shows an unexplained dip and then a rise to a leveling off point that is not present in the other curves. This behavior was reproducible but has not been explained. The 2-methyl-5-ethyl-pyridine proved to be the stronger base, probably due to inductive effects being stronger than steric effects.

The present results (Fig. 3 and 4) support the postulate of LUDER[9] that the high dielectric constant of the thionyl chloride promotes ionization of a salt composed of large ions.

SUMMARY

Conductance curves are presented for the reactions between organic bases and boron tribromide in the non-aqueous solvents, thionyl chloride, nitrobenzene and thiophosphoryl chloride. Interpretations of the data on the basis of the electronic theory are suggested. The reactions are stoichiometric and should find application in analytical chemistry.

RÉSUMÉ

Des courbes de conductance sont présentées pour les réactions se produisant entre les bases organiques et le tribromure de bore, dans les solvants non aqueux: chlorure de thionyle, nitrobenzène et chlorure de thiophosphoryle. Des interprétations des résultats sont proposées, se basant sur la théorie électronique. Les réactions sont stoechiométriques et peuvent être appliquées à la chimie analytique.

ZUSAMMENFASSUNG

Die Leitfähigkeitskurven der Reaktionen zwischen organischen Basen und Bortribromid in den nicht wässrigen Lösungsmitteln Thionylchlorid, Nitrobenzol und Thiophosphorylchlorid werden beschrieben. Die Ergebnisse werden auf Grund der Elektronentheorie ausgelegt. Die Reaktionen verlaufen stöchiometrisch und sollten in der analytischen Chemie Anwendung finden.

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HIGH FREQUENCY TITRATIONS OF SOME ORGANIC FUNCTIONAL GROUPS

by

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The determinations of functional groups in organic compounds is an important and common problem. Various chemical and physico-chemical methods have been proposed for determining amine, oxime, imine, carboxyl and other groups. The present study was undertaken in order to show the applicability of high frequency titrations for the determination of various functional groups both in aqueous and in non-aqueous solutions.

High frequency titrations hold considerable promise for use in studying non-aqueous or dilute aqueous systems. The systems being studied are completely isolated from electrodes and other active parts of the instrument and yet the instrument is itself responsive to slight changes in the composition of the system. High frequency methods have been established for use in determining various organic bases through studies made by WAGNER AND KAUFFMAN[1] and by MASUI[2] LANE[3] has described high-frequency titrations of organic bases, phenols and enols. The present study was initiated to investigate some of the broader aspects of high frequency titration for functional group analysis.

EXPERIMENTAL

Chemicals and reagents. All chemicals used were of reagent grade. Purities were checked by standard means, and where necessary, repurifications were carried out by appropriate methods.

Apparatus. A Sargent Model V Oscillometer was used for high frequency measurements. Hydrogen ion concentrations were determined by means of a Beckman Model G pH meter.

Titrations of acids

The carboxyl group may be titrated in either aqueous or non-aqueous media. In most cases, the carboxyl group tends to make compounds water soluble, but such solubility does not necessarily infer that water will be the best reaction medium. As a general rule, acids with very small dissociation constants should be titrated in a non-aqueous medium. The recommended procedure, however, is to first try the acid in aqueous solution to determine whether or not the end-point is sufficiently well defined to permit satisfactory titrations. If good end-points are not obtained, then the titrations should be carried out in pyridine, which has been found to be especially suitable for use in high frequency work.

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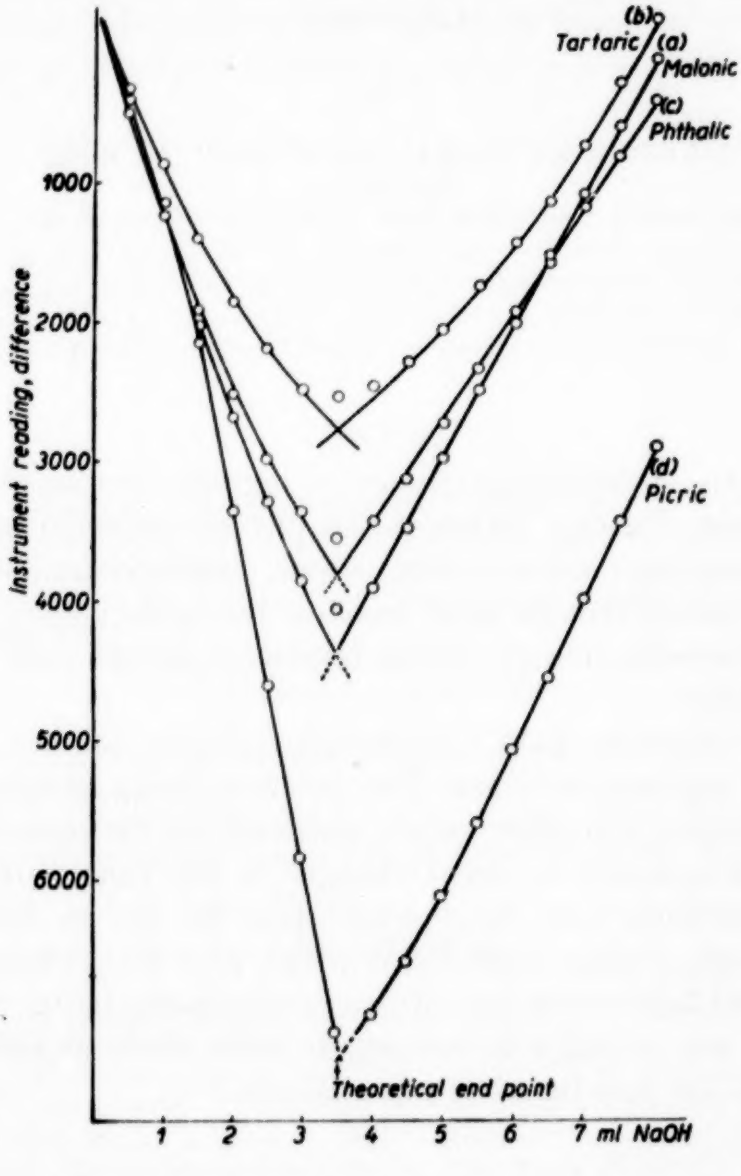


Fig. 1. Titrations of acids in aqueous solution.

Titration in aqueous solutions. For the purpose of determining the applicability of high frequency titrations of carboxylic acids in aqueous solution, exact amounts of selected acids were taken so as to obtain 1/1000M solutions. One hundred milliliters of the acid solution being studied were then transferred to the large titration cell of the Oscillometer and titrated with 0.0278 M sodium hydroxide. Titration curves are shown in Fig. 1 for malonic acid ($K_a = 1.6 \times 10^{-3}$ and 2.1×10^{-6}), tartaric acid ($K_a = 1.1 \times 10^{-3}$ and 6.9×10^{-5}), phthalic acid ($K_a = 1.26 \times 10^{-3}$ and 6.9×10^{-6}) and picric acid ($K_a = 1.6 \times 10^{-1}$). The curves for malonic, tartaric and phthalic acids show only one inflection point at 3.5 ml of sodium hydroxide. This volume of titrant represents one mol equivalent of base, indicating that only the first hydrogen can be titrated in aqueous solution and that the second hydrogen is too weak to be titrated under the conditions described. The titration curves for malonic and phthalic acids indicate a linear response for the instrument once the end-point has been reached. In the case of tartaric acid, the ascending portion of the titration curve exhibits a changing slope. This difference is probably due to the fact that the second dissociation constant for tartaric acid is greater than the second dissociation constant for malonic and phthalic acids. The second hydrogen probably is, therefore, partially neutralized in the case of tartaric acid. Picric acid shows a sharp inflection point at one mol equivalent of base.

Titrations in pyridine. Fritz and Lisicki[4] have proposed the titration of weak organic acids using sodium methoxide in benzene-methanol mixture. The course of the titration can be followed either by potentiometric methods or by the use of color indicators. These investigators have also suggested the use of basic solvents, such as butylamine and pyridine. Ishidate and Masui[5] used similar techniques for determining organic acids, but used high frequency oscillators for determining the end-points. The present study has indicated the suitability of pyridine as the solvent with alcoholic potassium hydroxide as titrant.

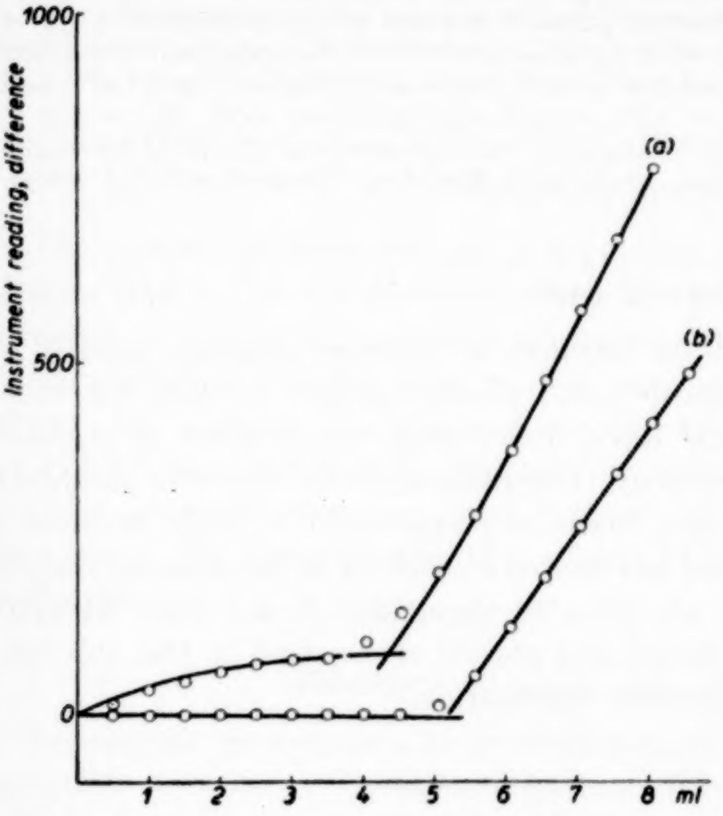


Fig. 2. Standardization of (a) alcoholic potassium hydroxide in pyridine against benzoic acid and (b) perchloric acid in acetic acid against potassium acid phthalate.

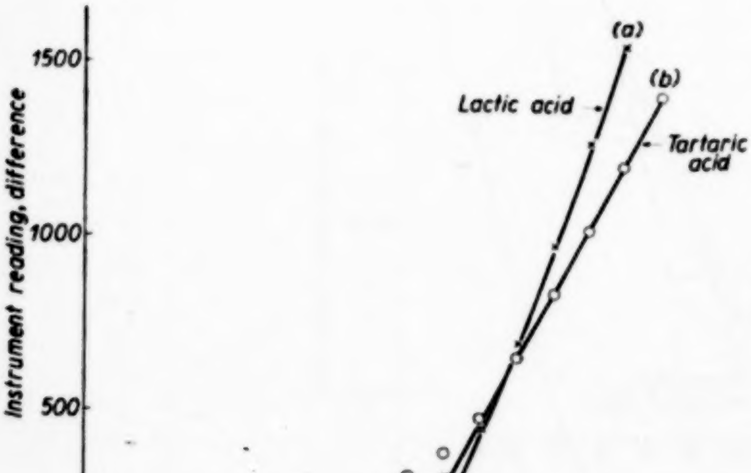


Fig. 3. Titrations of acids in pyridine with alcoholic potassium hydroxide.

Standardization of titrant. The alcoholic potassium hydroxide used as the titrant for organic acids was prepared by dissolving potassium hydroxide in absolute ethyl alcohol. The solution was kept in a bottle closed in such a way as to exclude carbon dioxide and water. Benzoic acid was found to be the most satisfactory primary standard for use in establishing the strength of the potassium hydroxide solution. The titration end-point, as determined by means of the Oscillometer, was well defined and reproducible. For the standardization, one hundred milliliters of pyridine were placed in the titration cell of the instrument. A weighed amount of primary standard benzoic acid was then dissolved in the pyridine and titrated with the alcoholic potassium hydroxide. The solution was stirred by means of an electric stirrer having a glass impeller. The presence of water in the solution must be avoided as much as possible because even trace amounts tend to introduce errors into the titration. Freshly prepared alcoholic potassium hydroxide should be used, and the pyridine should be repurified if it shows even the slightest discoloration. It should be noted that with the progress of the titration a precipitate of potassium benzoate separates from the solvent. This precipitation does not interfere with the titration and in fact, is necessary to the success of the method. Small amounts of water which might cause dissolution of the potassium benzoate convert the salt into the ionic form which results in serious loading of the Oscillometer.

Titration curves exhibit a slight rise during the initial stages of the titrations. This probably is due to the presence of trace amounts of water which dissolve some of the potassium benzoate that is first formed. The curves ultimately flatten until the end-point is reached, after which the curves rise steeply and approximately linearly. Curve (a) in Fig. 2 shows a titration curve obtained using 0.2442 g of benzoic acid dissolved in 100 ml of pyridine and titrated with 4.40 ml of 0.04545*M* alcoholic potassium hydroxide.

Titrations of acids. Titrations of acids in pyridine medium can be carried out using the same general procedure as that described for the standardization of the alcoholic potassium hydroxide against pure benzoic acid. The examples of such titrations are shown in Fig. 3. Using 0.09070*M* potassium hydroxide, 0.03950 g of lactic acid and 0.03320 g of tartaric acid were titrated (curves a and b respectively). In both cases the inflection point is marked at approximately 5 ml of titrant. Tartaric acid is titrated as a di-basic acid in pyridine medium. In the same way the determination of succinic acid ($K_a = 6.6 \times 10^{-5}$ and 2.8×10^{-6}), citric acid ($K_a = 1.76 \times 10^{-4}$ and 1.8×10^{-5} and 4.0×10^{-6}), formic acid ($K_a = 1.76 \times 10^{-4}$) and propionic acid ($K_a = 1.4 \times 10^{-5}$) were successfully carried out. The second hydrogen of succinic acid and the third hydrogen of citric acid were only partially titrated. These acids were, therefore, titrated as being monobasic and di-basic acids respectively.

Titrations of bases

Many organic bases are too weak to be titrated in aqueous solution, and it is recommended, therefore, that some suitable non-aqueous solvent be used for such titrations. CONANT, HALL, AND WERNER[6] have shown that the basicity of organic compounds is increased in acetic acid medium. Potentiometric or indicator methods for determining bases have been commonly made in acetic acid[7,8,9]. High frequency titrations of some bases have been carried out in acetic acid[1] or in benzene-methanol mixture[2]. In the present study, some analytically important bases were titrated using standard perchloric acid as the titrant and glacial acetic acid as the solvent. The method seems quite suitable for general application.

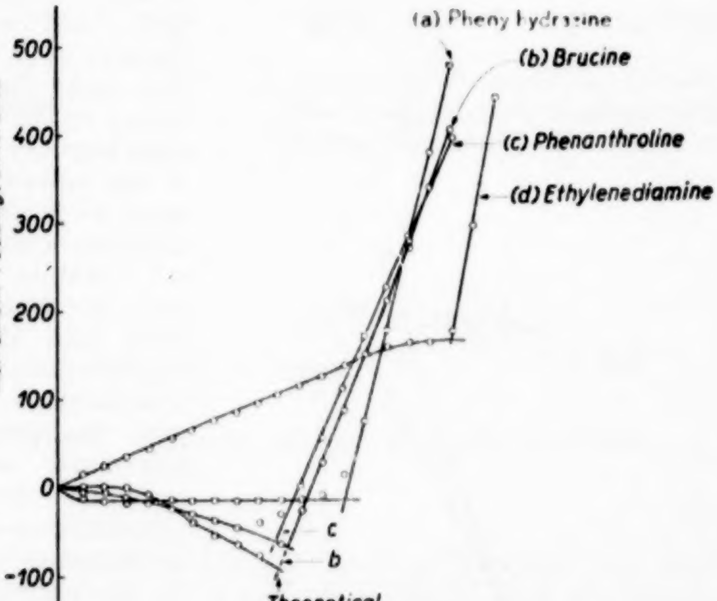


Fig. 4. Titrations of bases in acetic acid with perchloric acid.

Standardization of titrant. Perchloric acid of appropriate strength was prepared by simple dilution of the 70% acid using glacial acetic acid as the diluent. Standardization of the perchloric acid was made using potassium acid phthalate as the primary standard[1,9] and employing the Oscillometer for establishing titration end points. One hundred milliliters of glacial acetic acid were placed in the titration cell of the Oscillometer, and an appropriate amount of potassium acid phthalate was then added. The solution was stirred continuously during the titration with the perchloric acid. A typical titration curve is shown in Fig. 2, curve (b). The titration curves obtained in standardization employing the high frequency Oscillometer were well defined. Before the equivalence point, very little change in instrument response could be noted. After the equivalence point, the curves rose steeply giving well defined, reproducible end-points.

Determination. Titrations of bases were carried out in the same manner as that described under standardization. The titration of some typical organic bases is illustrated by the curves shown in Fig. 4. In each titration, well defined inflection points were obtained. The curves for brucine ($K_b = 7.2 \times 10^{-4}$ and 2.5×10^{-11}) and phenanthroline ($K_b = 1.1 \times 10^{-5}$) show one inflection point corresponding to one mol equivalent of titrant. A number of other bases were titrated with satisfactory accuracy. These include diethylamine ($K_b = 1.26 \times 10^{-3}$), *p*-toluidine ($K_b = 2.9 \times 10^{-9}$), *b*-naphthylamine ($K_b = 2 \times 10^{-10}$) and *o*-phenylenediamine ($K_b = 3.3 \times 10^{-10}$).

Titrations of imine groups

The acidity of imine groups is dependent upon the nature and position of other groups attached to the molecule. The imine group may act as a weak acid, and can be titrated as such using pyridine as the solvent. The procedure used in the high frequency studies was the same as that used in the titration of weak acids described above. Fig. 5 shows the results of one such titration. The end-points obtained are not as satisfactory as might be desired. Very distinct breaks in the titration curves are usually obtained, but the exact location of the end-point is somewhat uncertain because of the non-linearity of response exhibited, especially in the vicinity of the end-point.

Titrations of oxime and other chelating groups

Salinogenic groups may be so weakly acidic that they cannot be titrated directly in either aqueous or pyridine solutions. Where a donor group is located near the salinogenic group, it is often possible to carry out titrations by using a chelation

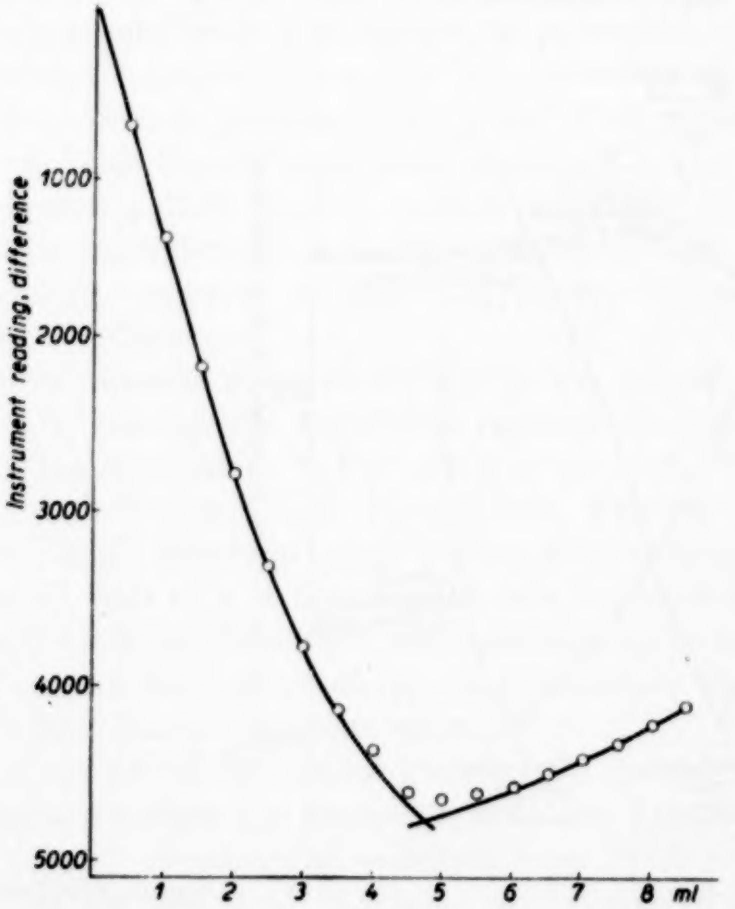
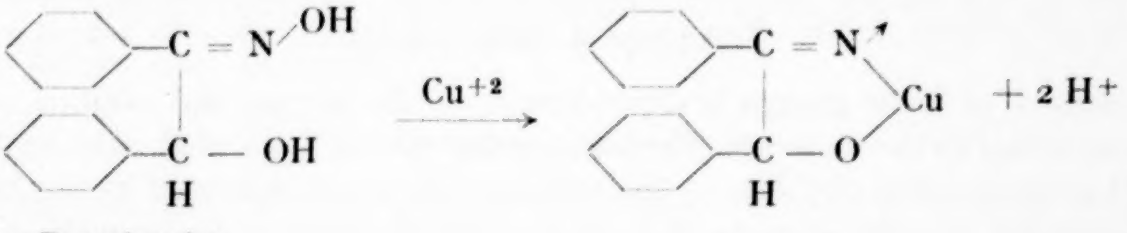
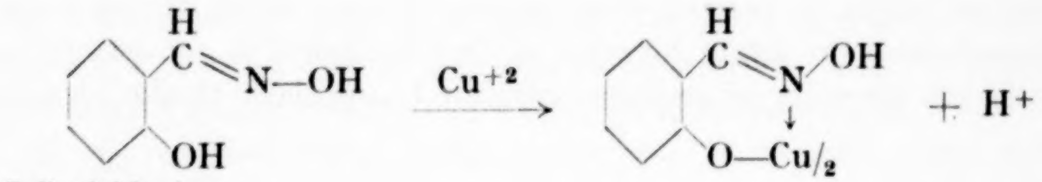


Fig. 5. Titration of dipicrylamine with KOH/alcohol in pyridine medium.

reaction to enhance the acidity. The oxime group, for example, can be titrated when a suitable metal is added, provided some second functional group is present and so located that chelate salts are formed. Upon chelation, one or more protons are liberated and these can then be titrated in aqueous solution using a standard base. The end-point can be determined accurately by means of a high frequency oscillator. As examples of such titrations, α-benzoinoxime and salicylaldoxime were determined. These compounds react with copper in the following manner:



α-Benzoinoxime



Salicylaldoxime

The liberated protons are completely dissociated so that in effect the chelation changes the organic reactants from very weak acids to strong acids. Fig. 6 shows titration curves obtained by titrating 0.001 molar solutions of α-benzoinoxime, nitroso-R-salt and salicylaldoxime.

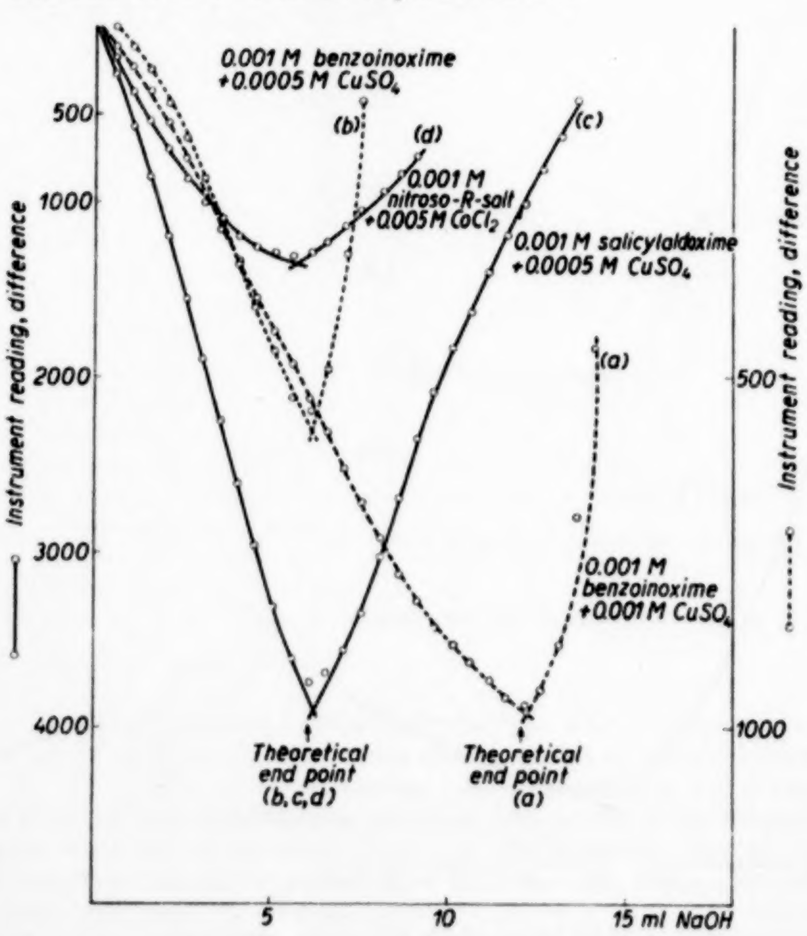
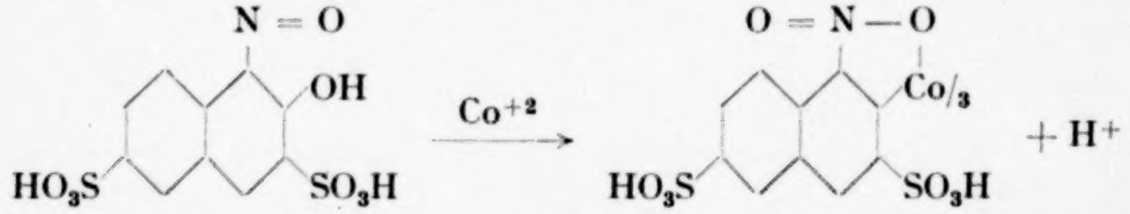


Fig. 6. Titrations of functional groups in the presence of metal salts.

The organic compounds were first dissolved in 25 ml of ethyl alcohol and subsequently diluted to 500 ml with distilled water. One hundred milliliters portions of these solutions were then placed in the titration cell of the Oscillometer, and copper sulfate was then added to liberate the hydrogen ions. The role of the metal is illustrated in the case of *α*-benzoinoxime. If the metal present is in excess, or in an amount equivalent to the chelating agent, the end-point obtained upon titration with standard sodium hydroxide falls at 2 mol equivalents (curve "a"). In curve "b", the mol equivalents of metal ion used was only half of the amount of chelating agent. The titration curve obtained in this case shows an end-point at 1 mol equivalent of sodium hydroxide, indicating that only half of the hydrogen had been released and that the other half could not be titrated under the conditions used. Curve "c" shows the result of a typical titration of salicylaldoxime containing one mol equivalent or more of copper ion. Only one hydrogen ion can be released by one mol equivalent of metal and additional metal does not, therefore, shift the position of the end-point.

Salinogenic groups other than the oxime group can be titrated by raising the reactivity through chelation. For example, nitroso-R-salt reacts with cobalt,



with the release of one proton for each molecule of chelating agent. The released hydrogen can be titrated in the manner described previously, and the titration curves have the general appearance of the one shown in curve "d" of Fig. 6.

DISCUSSION

Titrations of organic acids can be made using the high frequency oscillator as a means of detecting end-points. Such titrations can be performed in aqueous solution, provided the dissociation constant of the acid is in the order of 10^{-3}. For weaker acids, some basic solvent such as pyridine must be used. With pyridine as the solvent, it is possible to titrate acids having dissociation constants in the order of 10^{-5}. The usual precautions against carbon dioxide absorption should be observed. Other basic solvents, such as diethylamine and ethylenediamine, were investigated, but were found unsatisfactory because of their hygroscopic character, volatility, or loading effect on the Oscillometer.

Organic bases can be titrated using acetic acid as the solvent. The lowest limit of basicity that can be successfully titrated is represented by bases having dissociation constant of the order of 10^{-10}. For example, urea ($K_b = 1.5 \times 10^{-14}$) and thiourea ($K_b = 1.1 \times 10^{-15}$) could not be titrated. Brucine ($K_b = 7.2 \times 10^{-4}$ and 2.5×10^{-11}) gave a single inflection point, which is in agreement with the findings of FRITZ[7] who reported that only a single break was obtained when brucine was titrated in acetic acid medium. Similarly, phenanthroline gave only one inflection point. KOLTHOFF, LEE AND LEUSSING had reported previously that phenanthroline behaves as a monoacidic base in aqueous solution[10].

High frequency titrations of functional groups hold considerable promise. In the present study the application was limited to chelation. Liberated hydrogen ions were then titrated directly by means of standard base. With such reactions it is important to note that the course of chelation may be altered depending on the reaction environment. *α*-Benzoinoxime behaves as a di-basic acid in its reactions with copper[11]. Salicylaldoxime, on the other hand, is known to react in neutral or slightly acidic solution with the hydroxyl group serving as the salt forming grouping and the oxime group serving as a donor group. Inner complex salts are thereby formed and one hydrogen ion is released. In an ammoniacal solution, salicylaldoxime reacts to form a normal salt in which the hydroxyl group lends itself to salt formation, but the oxime group also reacts to form a normal salt with the replacement of a hydrogen ion. Under such conditions, a total of two protons are released.

The above reactions are cited merely to show that it may be necessary to know the reaction behavior of compounds being titrated. In most cases, the titrations are straight forward and a wide variety of compounds can be determined in the manner described. It is also possible that other reactions can be used in which standard solutions of metal ions are used as titrants and normal salt forming reactions, as well as inner-complex salt formation, can be followed by means of high frequency measurements.

ACKNOWLEDGEMENT

The authors wish to express their appreciation to E. H. SARGENT AND COMPANY for financial assistance during these studies.

SUMMARY

The high frequency titration of various organic acids and bases has been studied. The application of high frequency techniques in titrations of imine, oxime and other functional groups has been found useful. In general, these methods seem widely applicable in the determination of organic compounds and functional groups and can be used for the analysis of dilute systems.

RÉSUMÉ

Le titrage à haute fréquence de nombreux acides et bases organiques a été étudié. L'application des techniques à haute fréquence est avantageuse pour le titrage des groupements imine, oxime, etc. En général, ces méthodes semblent largement applicables au dosage de composés et de fonctions organiques et peuvent être utilisées pour l'analyse en solutions aqueuse et non-aqueuse.

ZUSAMMENFASSUNG

Die Hochfrequenz-Titration verschiedener organischer Säuren und Basen wurde untersucht. Die Anwendung von Hochfrequenz-Verfahren auf die Titration von Iminen, Oximen und anderen Funktionen wurde nützlich befunden. Im Allgemeinen können diese Methoden zur Bestimmung von organischen Verbindungen und funktionellen Gruppen und zur Analyse verdünnter Lösungen weitgehend angewendet werden.

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ARGENTIC OXIDE AS AN OXIDIMETRIC REAGENT

DETERMINATION OF MANGANESE, CERIUM AND CHROMIUM

by

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The +2 and +3 states of silver are among the strongest oxidants known in aqueous solution. From the excellent studies of NOYES and his coworkers[3] the formal potentials in 4*M* nitric acid at 25° are as follows (*vs.* the standard hydrogen electrode):

$$AgO^{+} + 2H^{+} + e = Ag^{+2} + H_2O \ ; E^f = 2.1 \text{ v.}$$

$$Ag^{+2} + e = Ag^{+} \ ; E^f = +1.929 \text{ v.}$$

Furthermore AgO^+ and Ag^{+2} are usually rapid in their oxidizing action. The use of silver ion as a catalyst in the persulfate oxidation of manganous ion to permanganate is a familiar example. These facts, coupled with the present commercial availability of argentic oxide, AgO, in a high state of purity (Merck and Co., Rahway, N.J.) prompted this study of argentic oxide as an oxidimetric reagent.

When argentic oxide is dissolved in cold nitric, perchloric, or sulfuric acid solutions of Mn^{+2}, Ce^{+3}, or Cr^{+3}, oxidation to MnO_4^-, Ce^{+4}, and $Cr_2O_7^{-2}$ occurs almost instantaneously. Since Ag^{+2} is reduced by water (at a rate which increases very greatly with temperature) its use as a standard solution for direct titrations is impractical. However, by simply adding a small excess of solid AgO to the cold test solution — the excess being easily recognizable by the characteristic brown color — and then warming for a few minutes, the excess Ag^{+2} is easily removed via reduction by water. The permanganate, ceric, or dichromate ion can then be titrated by any of the customary methods with a standard solution of a reductant (*e.g.*, ferrous ion).

Alternatively, after adding excess AgO the solution can be titrated potentiometrically with standard ferrous solution. Two inflections are observed, the first corresponding to reduction of the excess Ag^{+2} and the second to reduction of the MnO_4^-, Ce^{+4} or $Cr_2O_7^{-2}$.

Both of these techniques are simpler, and more rapidly executed, than the usual methods for determining these elements, and highly accurate results are easily attainable.

Reagents and standards

The argentic oxide used was a Merck product with a minimum AgO assay of 93%, the remainder being argentous oxide. This substance — which is manufactured chiefly for use in silver-zinc primary batteries — is a finely divided dark brown powder. The available evidence indicates that it is a true oxide of +2 silver and not a peroxide. It is stable indefinitely in the dry, solid state. It dissolves easily in dilute nitric or perchloric acids. The solutions in perchloric acid — in which the +2 silver probably exists chiefly as the aquo Ag^{+2} ion — are pale pink, but nitric acid solutions have an intense brown-black color due to a nitrate complex of +2 silver. Such solutions contain a very small proportion of +3 silver, formed by the slight disproportionation of the +2 silver

$$2\ Ag^{+2} + H_2O = AgO^+ + Ag^+ + 2\ H^+;\ K = ca.\ 10^{-3}$$

Small amounts of AgO also dissolve readily in dilute sulfuric acid, but addition of larger amounts results in the formation of a black precipitate. Although the composition of this precipitate is not known exactly, it probably contains a high proportion of +3 silver as Ag_2O_3. It dissolves readily via reduction by water when the solution is warmed.

From our experience the use of AgO as an oxidant presents no hazards in aqueous acid medium, and its reactions are smooth and rapid.

Standard manganese solutions in dilute sulfuric acid were prepared from manganous oxalate dihydrate of established purity as described by LINGANE AND KARPLUS[2].

A standard cerous solution in dilute sulfuric acid was prepared by reducing a standardized ceric sulfate solution (originally free from cerous ion) with a slight excess of hydrogen peroxide. A standard solution of +3 chromium in dilute sulfuric acid was prepared similarly by reducing a standard potassium dichromate solution with hydrogen peroxide.

Performance data

The oxidation of manganous, cerous, or chromic ion may be performed in either nitric, perchloric, or sulfuric acid solutions. However, nitric acid solutions are preferable because the intense brown color of the argentic nitrate complex serves to indicate when a small excess of argentic oxide has been added. The nitric acid concentration is not critical and may vary between 2 and $5M$. For the determination of manganese or cerium, the cold sample solution (volume *ca.* 50 ml and 2 to $5M$ in nitric acid) is treated with successive small portions of solid AgO until a small excess has been added. The solution is then diluted to *ca.* 150 ml with $1M$ sulfuric acid, heated to about 80° C, and (without further heating) allowed to stand until the excess +2 silver has been completely reduced by water. Fifteen minutes usually is adequate. The solution is finally titrated with a freshly standardized ferrous ammonium sulfate solution using *o*-phenanthroline ferrous ion as indicator in the usual way.

For the determination of chromium, the oxidation is done as above, but the final titration is performed by adding a small, measured excess of standard ferrous solution and back titrating either with a standard potassium dichromate solution using diphenylbenzidine sulfonate as indicator, or with a standard ceric solution and *o*-phenanthroline ferrous ion as indicator.

In determining manganese the heating of the solution to destroy the excess +2 silver must not be unduly prolonged, as this can cause significant reduction of permanganate ion by water. If the solution is heated initially to between 60° and 90°, and then removed from the source of heat, the excess +2 silver is all reduced within about 15 minutes, and the solution can stand at least 30 minutes without any appreciable reduction of permanganate ion. The time of standing is much less critical in the determination of cerium, and, of course, is quite immaterial in the case of chromium.

For the determination of up to 5 milliequivalents of manganese, cerium, or chromium, addition of 0.5 g of AgO usually is adequate. The theoretical amount of AgO for 5 milliequivalents is 0.31 g.

Red silver dichromate usually precipitates during the oxidation of chromium but this does no harm since it dissolves when the solution is diluted and warmed.

When the titration is performed potentiometrically destruction of the excess $+2$ silver by heating is unnecessary. In this case, after the cold test solution has been treated with a small excess of AgO it is simply diluted to 150 to 200 ml with 1M sulfuric acid, and titrated directly with the standard ferrous solution, using a platinum indicator electrode and a saturated calomel reference electrode. The potentiometric titration curve displays two inflections, the first after reduction of the excess $+2$ silver and the second after reduction of the permanganate, ceric, or dichromate ion. Typical potentiometric titration curves are shown in Fig. 1.

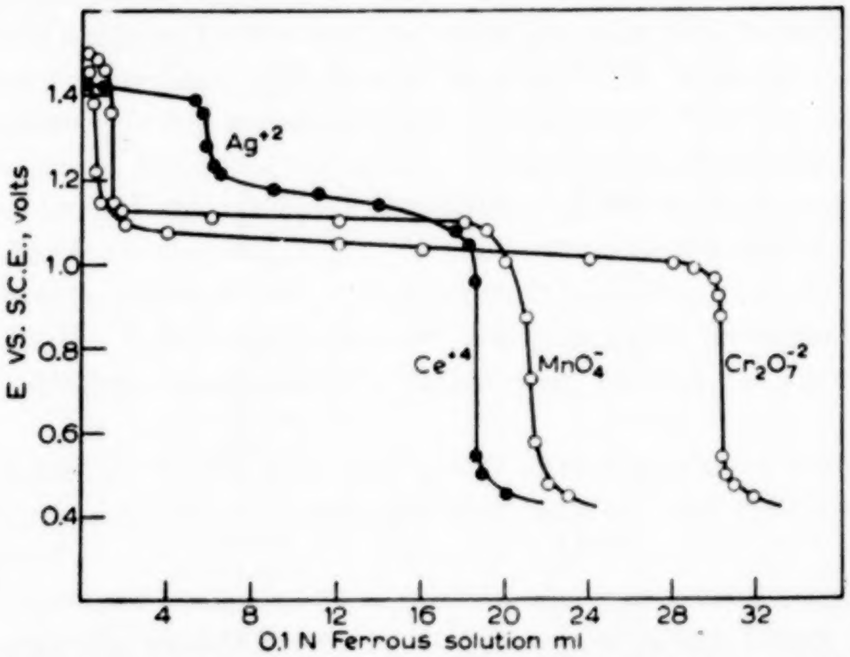

Fig. 1. Typical potentiometric titration curves of solutions of manganese, cerium and chromium after oxidation with excess argentic oxide.

Steady potentials are established quickly, so that the potentiometric titration can be performed expeditiously simply by titrating to the two successive equivalence point potentials. The most elegant and rapid procedure is to employ an automatic titrator[1], in which case the oxidation and titration can be completed in about 10 minutes.

When chromium is being determined by the potentiometric method any reddish precipitate of silver dichromate should be dissolved by warming the solution to about 40° before beginning the titration. When titrations were begun without first dissolving the silver dichromate positive errors of 0.6 to 1% were observed. Apparently the silver dichromate coprecipitates a small amount of $+2$ and/or $+3$ silver, perhaps as argentic dichromate.

The performance data in Table I demonstrate that all three elements are determinable with an average error and precision within ±0.2%.

The foregoing procedures have also been successfully applied to the analysis of various aluminium and ferrous alloys containing manganese and chromium. When a little hydrochloric acid is needed to dissolve the alloy, the sample solution is evaporated down with sulfuric acid to remove the chloride and is then taken up in dilute nitric acid before the oxidation with AgO. Removal of the last traces of chloride is not

TABLE I

TYPICAL PERFORMANCE DATA

Element	*Taken* *mg*	*Found* *mg*	*Error* *%*
Manganese	39.06	39.03	−0.1
		39.00	−0.2
		39.08[a]	+0.1
	15.63	15.60	−0.2
		15.59	−0.3
		15.63[a]	0.0
Cerium	359.8	360.1	+0.1
		358.7	−0.3
		360.5[a]	+0.2
	143.9	144.1	+0.1
		143.9	0.0
		143.8[a]	−0.1
		144.2[a]	+0.2
Chromium	256.6	257.0[a]	+0.2
		257.2[a]	+0.2
		257.2[a]	+0.2
		256.6[a]	0.0
		256.2[a]	−0.2
	42.37	42.28	−0.2
		42.30	−0.2
		42.39	0.0
		42.32	−0.1
	8.463	8.456	−0.1
		8.443	−0.2
		8.431	−0.4

[a] These values by potentiometric titration. All others by visual titration.

necessary, since any remaining precipitates as silver chloride which does not interfere. Chloride in amounts up to at least 20 mg causes no error. This is one of the several advantages of this method over the persulfate and bismuthate methods, which demand complete absence of chloride.

When this method was applied to Bureau of Standards Ferromanganese 68a, the percentages of manganese found in two trials were 80.01% and 80.33%, in very good agreement with the certified value of 80.07%. The average value by the present method (80.17%) also agrees excellently with the value (80.12%) determined for this same sample by LINGANE AND KARPLUS[2] by the permanganimetric-pyrophosphate method. The latter is the most precise method of manganese determination, and it is superior to the bismuthate method on which the Bureau's value is based.

The *sum* of manganese and chromium evaluated by the present method in Bureau of Standards Aluminium Alloy 85a (1.58% Mn and 0.231% Cr) agreed to 1 part per thousand with the Bureau's values. Results correct to 4 parts per thousand were obtained for the sum of manganese and chromium in Bureau of Standards Steel 135 (0.575% Mn and 5.15% Cr). The sum of manganese and chromium was determined in Bureau of Standards Manganese Rail Steel 100 (1.38% Mn and 0.18% Cr) with an average error of 1 part per thousand in two trials.

The determination of cerium in misch metal (alloy of cerium and other rare earth metals) was also performed with excellent results. A sample of misch metal, supplied by the Mallinckrodt Chemical Works, was simply dissolved in $2M$ nitric acid and the present method applied. The cerium values found in three trials were 45.05, 44.93, and 44.95%, compared to the value 44.97% (determined by the persulfate method) furnished with the sample.

The present method is applicable in the presence of most of the elements likely to be associated with manganese, cerium, and chromium. Vanadium is oxidized to the $+5$ state and reduced by ferrous ion. However, by adding a measured excess of standard ferrous solution to the oxidized solution, and back titrating with standard ceric solution, any vanadium will finally be converted back to the $+5$ state and should not interfere. Direct potentiometric titration of ceric ion or permanganate ion with ferrous ion in the presence of $+5$ vanadium is, of course, also applicable and if desired the vanadium can be titrated subsequent to the manganese or cerium.

Cobalt is oxidized to the $+3$ state, but is completely reduced again by water when the solution is warmed, so it should not interfere (*vide infra*).

As discussed in the following paragraph, thallium can be expected to interfere, but it is not a common companion to manganese, cerium, or chromium.

Attempted determination of thallium and cobalt. Attempts were made to apply the argentic oxide method to the determination of thallium and cobalt, but these trials were not successful.

In nitric acid medium thallous ion is rapidly and apparently completely oxidized on addition of argentic oxide. However, a black precipitate forms and qualitative tests demonstrated that this contained both thallium and silver. Since the precipitate forms only after excess argentic oxide is added, it presumably contains thallium in the $+3$ state and silver in either the $+2$ or $+3$ states. NOYES *et al.*[3] successfully employed oxidation of thallous ion to thallic ion for the assay of solutions of $+2$ silver. This succeeds because excess thallous ion is present, and the black precipitate is not formed.

Cobaltous ion in dilute nitric acid is rapidly oxidized to the cobaltic state. However, cobaltic ion is reduced too rapidly by water to permit destruction of the excess $+2$ silver by warming the solution. The potentiometric technique also fails because the potential of the cobaltic-cobaltous couple is only about 0.1 v less oxidizing than the argentic-argentous couple, so that a distinct potential break is not observed for the titration of argentic ion in the presence of cobaltic ion.

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SUMMARY

Argentic oxide, AgO, is commercially available (Merck) in pure form, and it serves advantageously as a very powerful oxidimetric reagent in acid media. On addition of a small excess of argentic oxide to cold solutions of manganous, cerous, or chromic ion in 2 to $5M$ nitric acid rapid and complete oxidation to permanganate, ceric, or dichromate ion takes place, and the excess

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argentic oxide dissolves. By simply diluting and warming the solution for a few minutes the excess +2 silver is completely reduced by water, and the permanganate, ceric, or dichromate ion can then be titrated with standard ferrous solution in the usual way.

Alternatively the titration with ferrous solution can be performed potentiometrically, which leads to an even simpler procedure because destruction of the excess +2 silver by heating is unnecessary. The potentiometric titration curve exhibits two inflections, the first after reduction of the excess +2 silver and the second after reduction of the permanganate, ceric, or dichromate ion.

Results precise and accurate to ±0.2% or better are easily obtained by either of these procedures, and they are more convenient and rapid than the classical titrimetric methods of determining these elements. The method has been applied with excellent results to the determination of managanese and chromium in aluminium and ferrous alloys, and to the determination of cerium in misch metal.

RÉSUMÉ

L'oxyde d'argent(II), AgO, peut être obtenu dans le commerce (Merck) à l'état pur et il peut être utilisé avantageusement comme oxydant énergique en milieu acide. Par addition d'un léger excès d'oxyde d'argent(II) à des solutions froides de manganèse(II), de cérium(III) ou de chrome (III) dans l'acide nitrique 2 à 5*M*, une oxydation rapide et quantitative en permanganate, cérium (IV) et dichromate se produit; l'excès d'oxyde d'argent se dissout. Par simple dilution et chauffage de la solution pendant quelques minutes, l'excès d'argent(II) est complètement réduit par l'eau, et les ions permanganique, cérique et dichromique peuvent être ensuite titrés par une solution étalon de fer(II) par le procédé habituel.

D'autre part, le titrage par le fer(II) peut être effectué par potentiométrie, ce qui constitue un procédé encore plus simple, la destruction de l'excès d'argent(II) par chauffage n'étant pas nécessaire. La courbe de titrage potentiométrique présente deux inflections, la première après réduction de l'excès d'argent(II) et la seconde, après réduction des ions permanganique, cérique ou dichromique.

On obtient facilement des résultats précis, à ±0.2%. Ces deux procédés sont plus pratiques et plus rapides que les méthodes classiques de dosage volumétrique de ces éléments. La méthode décrite a été appliquée avec succès au dosage du manganèse et du chrome dans les alliages de l'aluminium et du fer, ainsi qu'au dosage du cérium dans un alliage avec d'autres éléments des terres rares.

ZUSAMMENFASSUNG

Silber(II)-oxyd, AgO, ist in reiner Form im Handel (Merck) und kann in saurer Lösung als sehr energisches oxydimetrisches Reagenz dienen. Fügt man einen kleinen Überschuss von AgO zu einer kalten Lösung von Mangan(II), Cer(III) oder Chrom(III) in 2-5*M* Salpetersäure, so findet eine rasche und vollständige Oxydation zu Permanganat, Cer(IV) oder Dichromat statt, während das überschüssige AgO sich löst. Durch Verdünnen und Erwärmen der Lösung während ein paar Minuten wird das überschüssige Silber(II) vollkommen durch Wasser reduziert, wonach die Permanganat-, Cer(IV)- oder Dichromationen mit einer Eisen(II)-Titerlösung wie üblich titriert werden können.

Die Titration mit Eisen(II)-Lösung kann auch potentiometrisch erfolgen, was einfacher ist, da sich die Zerstörung des überschüssigen Silber(II) erübrigt. Die potentiometrische Titrationskurve zeigt zwei Wendepunkte, einen nach Reduktion des überschüssigen Silber(II) und einen nach Reduktion des Permanganat-, Cer(IV)- oder Dichromations.

Man erhält nach beiden Verfahren leicht Ergebnisse mit einer Genauigkeit von mindestens ±0.2%. Diese Methode ist besser und rascher als die klassischen titrimetrischen Bestimmungsmethoden der genannten Elemente. Sie wurde mit ausgezeichnetem Resultat zur Bestimmung von Mangan und Chrom in Aluminium- und Eisenlegierungen und von Cer in „Mischmetall" (Cer mit anderen seltenen Erden) angewendet.

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MICRO-ELECTROLYTIC DETERMINATION OF LEAD AND ITS APPLICATION TO THE ANALYSIS OF TIN-BASE AND LEAD-BASE ALLOYS

by

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INTRODUCTION

Continuing our search for suitable micro-determinations of the constituents of tin-base and lead-base alloys[1,2,3,4,5], we considered the examination of the possibility of determining lead by micro-electrodeposition as worth while, and started with a bibliographic survey of the problem. Without enumerating all of the references, mention must be made of some of the methods found, *e.g.* the anodic electrodeposition of lead as PbO_2, its redissolution and final determination as $PbSO_4$[6,7], the electrolytic separation of lead from zinc or nickel and its subsequent iodometric determination[8], the anodic electrodeposition as PbO_2 and its determination in this form[9,10,11], and the cathodic electrodeposition as lead metal[12].

Notwithstanding the abundance of bibliographic resources, the application of the existing methods to the electrolytic determination of lead in tin-base and lead-base alloys, presented, *a priori*, certain difficulties and inconveniences. We have, consequently, decided to re-examine the problem of the micro-electrodeposition of lead systematically; this led us to evolve a simple and exact method, which we later applied successfully to the analysis of the a.m. alloys.

Principle of the method

Lead is deposited electrolytically, in the CLARKE-HERMANCE micro-electrolytic outfit[13], as PbO_2 on the platinum anode, from a hot nitric acid solution containing urea to remove traces of nitrous acid. After drying at 120° C, the PbO_2 deposit is weighed and lead is calculated from it, using the theoretic factor of 0.8662.

EXPERIMENTAL

Reagents and standard solutions employed

1. Lead nitrate solution (prepared by dissolving 2 g of pure lead metal in conc. nitric acid, evaporating excess acid and making up to 1 litre with bi-distilled water. The solution therefore contained 2 mg lead per ml).
2. Nitric acid (1:1), freshly boiled to remove nitrous acid.
3. Urea.
4. Alcohol, 96%.
5. Hydrogen peroxide, 30%.
6. Hydrochloric acid, conc.
7. Sodium sulphide solution, 30% (prepared by dissolving 30 g of $Na_2S.9H_2O$ in 100 ml bi-distilled water).

8. Sodium hydroxide solution, 30%.
9. 1% phenolphtalein (alcoholic solution).
10. Wash mixture A (prepared by adding 3 ml each of reagents No. 7 and No. 8 to 100 ml bi-distilled water).
11. Nitric acid (1:3).
12. Wash mixture B (HNO_3 1:10).
13. Copper nitrate solution (prepared by dissolving 1 g approx. of pure copper metal in conc. nitric acid, evaporating excess acid and making up to 1 litre with bi-distilled water. The solution therefore contained 1 mg copper per ml approx.).
14. Bi-distilled water was used throughout.

The following procedure for the determination of lead by electrodeposition as PbO_2 from pure lead nitrate solution was evolved, after investigation of the factors affecting it: amount of lead, the total volume of the sample, acidity, temperature at which electrolysis is carried out, duration of electrolysis, temperature and duration of electrode drying and presence of copper in sample.

Procedure recommended for the determination of lead from lead nitrate solution

1-5 ml of lead nitrate solution, containing 2-10 mg of lead, are introduced into a CLARKE-HERMANCE electrolytic cell[13]; 2 ml nitric acid (1:1) are added and the volume made up to 6-7 ml with bi-distilled water (if necessary). 30-50 mg of urea are added, the water in the heating jacket of the cell is heated to 80°-90° C, and the solution kept stirred by a moderate stream of air bubbles. The outer net electrode is connected as anode and electrolysis commenced at 1.8-2.0 V (the temperature of the water jacket being kept at 80-90° C throughout the determination). After 10 minutes, the inside of the electrolytic cell is rinsed down with 2 ml of bi-distilled water and electrolysis continued for 5 minutes more. The air capillary is removed, the stopcock opened and the solution allowed to drain from the cell; at the same time, the cell and electrodes are washed with a continuous stream of alcohol from a small wash bottle. The current is stopped, the anode removed, dipped into alcohol and dried in a drying oven at 120° C for 5 minutes. The anode is next removed from the oven, cooled for 5 minutes on a nickel block outside the micro-balance, left for 5 minutes on the pan of the balance and weighed in the 10th minute. The PbO_2 deposit is dissolved by dipping the anode into a beaker containing nitric acid (1:1) and a little hydrogen peroxide, 30%; the electrode is rinsed, first with bi-distilled water and then with alcohol, dried and weighed as above.

The difference of the two weighings multiplied by 0.8662 (theoretic factor Pb/PbO_2) gives the amount of lead present in the sample.

The time required for 1 determination is 50 minutes to 1 hour approx.

The results obtained are given in Table I.

TABLE I

MICRO-ELECTROLYTIC DETERMINATION OF LEAD FROM LEAD NITRATE SOLUTION

Exp. No.	*Duration of electrolysis* *min*	*Pb present* *mg*	*PbO_2 found* *mg*	*Pb calculated* *mg*	*Pb difference* *mg*	*Relative error* %
1	15	2.000	2.297	1.990	—0.010	—0.5
2	15	2.000	2.303	1.995	—0.005	—0.25
3	15	3.000	3.469	3.005	+0.005	+0.17
4	15	3.000	3.455	2.993	—0.007	—0.2
5	15	4.000	4.630	4.011	+0.011	+0.3
6	15	4.000	4.594	3.979	—0.021	—0.5
7	15	5.000	5.779	5.006	+0.006	+0.1
8	15	5.000	5.755	4.985	—0.015	—0.3
9	15	7.500	8.644	7.487	—0.013	—0.2
10	15	7.500	8.640	7.484	—0.016	—0.2
11	15	10.000	11.533	9.990	—0.010	—0.1
12	15	10.000	11.539	9.995	—0.005	—0.05
13	30	1.000	1.145	0.992	—0.008	—0.8
14	30	1.000	1.152	0.998	—0.002	—0.2
15	30	1.000	1.150	0.996	—0.004	—0.4
16	15	1.000	1.001	0.867	—0.133	—13.3
17	15	1.000	1.093	0.947	—0.053	—5.3

Conclusion

As indicated by Table I, results are exact (maximum relative error: ± 0.5% for 2-10 mg of lead; exp. No. 1-12). For 1 mg of lead, the maximum relative error reaches ± 0.8%, due to the small amount of lead (exp. No. 13-15), provided electrolysis is prolonged to 30 minutes (see DISCUSSION I, pt. 1).

Exp. No. 16-17 prove that for 1 mg of lead, a time of electrolysis of 15 minutes is decidedly insufficient.

DISCUSSION I

1. As can be seen from Table I, the above method was tested on samples containing 1-10 mg of lead; for 2-10 mg of lead, results were exact: ± 0.5% maximum relative error; for samples of 1 mg, results were low, but could be improved by prolonging the electrolysis to 30 minutes, rinsing after 25 minutes (maximum relative error ± 0.8%).

2. The time required for drying and cooling both the empty electrode and the electrode coated with the PbO_2 deposit was tested. The schedule of 5 minutes drying, 5 minutes cooling on the nickel block and 5 minutes on the pan of the balance was found satisfactory in both cases. Additional drying caused no change in weight.

3. The temperature of 120° C was found adequate for drying the electrode and deposit.

4. The measurements of the Clarke-Hermance electrolytic cell used made 6-9 ml the convenient limits of total sample volume.

5. Keeping the temperature of the sample solution at about 80° C during electrolysis is important with a view to preventing any lead from being deposited cathodically, obtaining a deposit which adheres well to the anode and hastening complete electrodeposition of the lead[14]. Incidentally, the vapors evolved through this heating, condense partially on the cooler upper part of the electrolysis vessel, and thus provide a continuous rinsing effect.

6. No improvement of results was obtained by prolonging electrolysis beyond the 15 minutes recommended in the procedure described above (except for 1 mg samples; see pt. 1 of this discussion).

7. The acidity of the sample solution was tested; it was found inadvisable to let it rise above 15% volume conc. nitric acid approx.; where higher acidity was employed, partial dissolution of the PbO_2 deposited could be observed, accompanied by increased evolution of gas, rising current, and causing low results.

8. The addition of copper nitrate solution in amounts up to 1 mg was tested; this had no influence on results, which remained good.

9. It was found advisable to weigh the empty anode after the dissolution of the lead dioxide deposit; if this is done, any platinum lost during electrolysis does not affect the results of the lead determination.

10. The pumping tube supplied with the micro-electrolytic outfit described caused inconvenient bending of the stems of the platinum electrodes; we therefore substituted a plain capillary tube.

11. Macro-methods encountered in literature, dealing with the anodic electrodeposition of lead as PbO_2, recommend various empirical factors for the calculation of lead from PbO_2 deposited, depending on the amount of lead determined, temperature and time of drying of the deposit, *etc*. Under the conditions recommended in our procedure, exact results are obtained using the theoretic factor of 0.8662.

APPLICATION OF THE METHOD TO THE DETERMINATION OF LEAD IN TIN-BASE AND LEAD-BASE ALLOYS

Rough attempts to apply the method described above directly to alloys containing tin, lead, antimony and copper, by dissolving the alloy in nitric acid, without resorting to the preliminary separation of tin and antimony, indicated that this was impracticable, due to the high results obtained through their presence.

Separation of tin and antimony, after evaporation of the nitric acid, fails to remove the antimony quantitatively, while presumably causing some lead to be retained in the precipitated antimony oxide and metastannic acid.

Antimony is partially co-deposited anodically with lead peroxide and must therefore be separated from the lead before the electrolytic determination of the latter.

A sulphide separation was therefore evolved, to separate lead and copper from antimony and tin. This can be applied successfully to alloys containing 100%-5% lead, and varying amounts of tin, antimony and copper.

Recommended procedure

5-100 mg of the alloy (containing 2-10 mg of lead) are weighed into a short Pyrex test tube (approx. dimensions: height 90 mm, diameter 15 mm, approx. useful volume 10 ml) provided with a loosely fitting glass stopper. 0.5-1.0 ml of conc. hydrochloric acid are introduced and the stopper replaced at once. After the initial effervescence has subsided, 5-10 drops of hydrogen peroxide, 30%, are carefully added and the test tube kept in a nearly boiling water bath until complete solution of the alloy has been achieved. If necessary, additional hydrogen peroxide is added; before its addition, the test tube must be removed from the water bath and cooled. The solution is cautiously boiled for a short time to destroy excess hydrogen peroxide and expel chlorine. The test tube is cooled, the stopper rinsed into the tube with 0.5-1.5 ml of sodium sulphide solution, 30%, by means of a capillary dropper, a drop of 1% phenolphtalein solution added and a sodium hydroxide solution, 30%, pipetted into the tube until a reddish coloration is obtained. Throughout these additions the tube is shaken periodically to ensure proper mixing. Another 0.5-1.0 ml of the sodium sulphide solution are now added, the tube closed with the stopper and placed in a boiling water bath for approx. 15 minutes, until the black copper sulphide

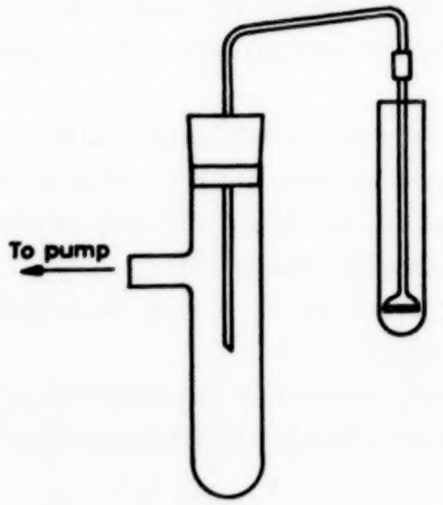

Fig. 1. Apparatus for filtration.

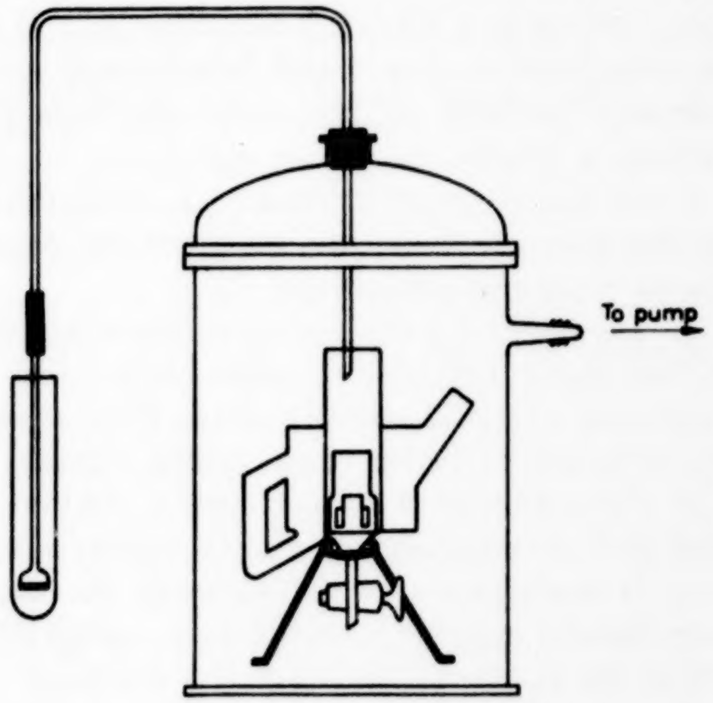

Fig. 2. Apparatus for filtration.

References p. 212

and lead sulphide precipitate settles on the bottom of the tube and the solution above it clears. (Should brown tin sulphide be still visible, additional sodium sulphide solution must be added.)

The precipitate is now filtered, using a medium porosity glass filterstick* (Fig. 1) and washed 3-4 times with 3-4 ml of wash mixture A, using low suction. The filterstick is now detached from the suction line, test tube and filterstick washed down with 2 ml of freshly boiled nitric acid (1:3), the test tube placed in a nearly boiling water bath and kept in it until the precipitate dissolves completely (some sulphur appears at this stage). The electrolytic cell is placed inside a filter-bell (Fig. 2) and the filterstick connected to the suction device. The solution is filtered into the electrolytic cell, the tube and filterstick washed with 5 portions of 1 ml each of wash mixture B (freshly boiled), each time sucking the wash liquid into the electrolytic cell. The filterstick is detached from the suction device, the electrolytic cell removed from the filter-bell and replaced in its stand, 1 ml of copper nitrate solution (1 mg copper) added and electrolysis carried out as indicated in: "*Procedure recommended for the determination of lead from lead nitrate solution*", starting from: "30-50 mg of urea are added..." (p. 208).

The time required for one determination is 2-2$^1/_2$ hours approx.

The results obtained are given in Table III. Table II indicates the composition of the alloys which were used to test the procedure described above.

TABLE II

Alloy No.	*Pb* %	*Sn* %	*Sb* %	*Cu* %	*Fe* %	*Ni* %	*Bi* %	*As* %
1	5.16	85.7	7.16	2.0				
2	28.9	the rest						
3	72.5	9.4	18.04					
4	84.285	5.16	10.20	0.124	the rest			

TABLE III

MICRO-ELECTROLYTIC DETERMINATION OF LEAD IN TIN-BASE AND LEAD-BASE ALLOYS

Exp. No.	*Alloy No.*	*Alloy mg*	*Pb present mg*	*Pb found mg*	*Pb difference mg*	*Pb theoretical %*	*Pb found %*	*Difference %*	*Relative error %*
1	1	100.000	5.160	5.141	—0.019	5.16	5.14	—0.02	—0.4
2	1	100.000	5.160	5.175	+0.015	5.16	5.175	+0.015	+0.3
3	2	21.350	6.170	6.134	—0.036	28.9	28.73	—0.17	—0.6
4	2	10.052	2.905	2.918	+0.013	28.9	29.03	+0.13	+0.4
5	3	10.305	7.471	7.485	+0.014	72.5	72.63	+0.13	+0.2
6	3	5.012	3.634	3.614	—0.020	72.5	72.11	—0.39	—0.6
7	4	12.105	10.203	10.192	—0.011	84.285	84.20	—0.085	—0.1
8	4	5.321	4.485	4.460	—0.025	84.285	83.82	—0.47	—0.6

Conclusion: As indicated by Table III, results are exact (maximum relative error: ± 0.6%).

DISCUSSION II

1. The chlorine evolved during the solution of the alloy often leads to appreciable spattering; the test tube used, with its loosely fitting stopper, effectively prevented ejection losses, while allowing the escape of gases and vapors.

2. For alloys containing 100%-30% of lead, 0.5 ml of conc. hydrochloric acid is sufficient for effecting solution; for alloys containing 30%-5% of lead, 1.0 ml must be employed.

3. For alloys containing 100%-30% of lead, 0.5 ml of sodium sulphide solution,

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* The dimensions of the filterstick used were: overall diameter 10 mm; stem diameter 4 mm; overall height 110 mm. All filtersticks used were U.S.A. produce, made by Corning Glass Works.

30%, is used to rinse the stopper and another 0.5 ml added after the addition of sodium hydroxide solution, 30%; for alloys containing 30%-5% of lead, 1.5 ml must be used initially and 1.0 ml or more added finally, as required in each case to achieve a clear solution above the black sulphide precipitate.

4. It is important to add sodium sulphide before adding sodium hydroxide; where this is neglected, a precipitate of sodium pyroantimonate may form[15], which does not subsequently dissolve in sodium sulphide.

5. Thorough washing of the copper and lead sulphides precipitate is indicated to effect as complete a removal of chloride ions as possible. This is important, as the presence of chloride ions during the subsequent electrolysis favors the cathodic deposition of lead.

6. The copper and lead sulphides are dissolved in dilute nitric acid (1:3) and warmed carefully to prevent any lead sulphide from being oxidized to lead sulphate, thus causing losses.

7. Cathodic deposition of lead (see pt. 5 above) is prevented by carrying out the electrolysis at 80° C, keeping the amount of nitric acid present sufficiently high (15% volume approx.) and adding copper nitrate solution.

SUMMARY

The authors have developed an exact micro-method for the determination of lead by anodic electrodeposition as lead dioxide. The method has been successfully applied to the determination of lead in tin-base and lead-base alloys.

RÉSUMÉ

Les auteurs ont élaboré une micro-méthode électrolytique exacte pour le dosage du plomb à l'état de PbO_2. Ils ont appliqué la méthode établie au dosage du plomb dans les alliages à base d'étain et de plomb.

ZUSAMMENFASSUNG

Die Verfasser haben eine genaue Mikromethode zur elektrolytischen Bestimmung des Bleis als Bleidioxid an der Anode ausgearbeitet. Die Methode wurde erfolgreich zur Bestimmung des Bleis in Blei- und Zinn-Legierungen angewendet.

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MICRO-GRAVIMETRIC DETERMINATION OF THALLIUM WITH THIONALIDE

by

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INTRODUCTION

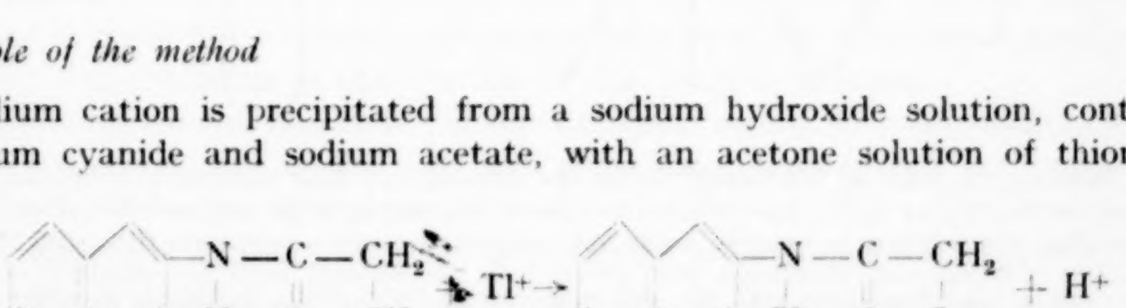
In the course of our systematic search for suitable micro-determinations in the field of inorganic analysis, the existing micro-methods for the determination of thallium were reviewed. Without enumerating all the references, mention must be made of some of the method found, *e.g.*: a) titrimetric method using ethylenediamine tetraacetic acid[1], b) titrimetric method employing the liberation of iodine[2], c) micro-gravimetric determination as thallochromate[3], d) potentiometric titration by oxidation with $KBrO_3$[4], e) potentiometric titration by oxidation with $KMnO_4$[5], f) various additional instrumental methods mentioned in a recent review of detection and determination of thallium[6].

After completion of the a.m. review, it was still considered desirable to evolve an exact micro-gravimetric method for the determination of thallium with thionalide (β-aminonaphthalide of thioglycollic acid), this reagent having proved adequate for the micro-determination of lead[7,8]. The macro-method has been proposed by BERG[9].

To that end, the various factors affecting this determination, such as: 1) the amount of thallium, 2) the amount of reagent and the method of its introduction, 3) the wash liquids used, 4) the temperature and the time required to dry the precipitate, were studied. Based on these investigations, an exact micro-gravimetric method has been developed, applying EMICH's[10] micro-technique and using a porcelain filterstick.

Principle of the method

Thallium cation is precipitated from a sodium hydroxide solution, containing potassium cyanide and sodium acetate, with an acetone solution of thionalide:



The filtered and washed precipitate is dried at 110° C[11]. Thallium is calculated from the weight of the precipitate obtained.

EXPERIMENTAL

Reagents and solutions employed

1. Thallium sulphate solution (prepared by dissolving 2.470 g of pure thallium sulphate in bi-distilled water and making up to 1 litre with bi-distilled water. The solution, therefore, contained 2 mg of thallium per ml).
2. Sodium acetate solution, 10%.
3. Potassium cyanide solution, 20%.
4. Sodium hydroxide solution 2*N*.
5. Thionalide.
6. Acetone.
7. A mixture of 20 ml acetone, 20 ml bi-distilled water and 3 ml ammonium hydroxide conc. (the pH of this mixture should be 8.5 approx.).
8. A mixture of 20 ml acetone, 20 ml bi-distilled water and one drop of sodium hydroxide 2*N* (the pH of this mixture should be 8.5 approx.).
9. Acetone-water (mixture 1:1).
10. Iodine solution 0.1*N*.
11. Sulphuric acid (1:5).
12. Bi-distilled water was used throughout.

Procedure recommended for the micro-gravimetric determination of thallium

The solution containing the thallium cation (3-6 mg thallium in 1-3 ml) is introduced into a previously dried and weighed Pyrex glass micro-beaker (dimensions of the beaker: height 55 mm, outer diameter 18 mm). To this solution are added 0.5 ml of sodium acetate solution, 10%, 0.25 ml of potassium cyanide solution, 20% and 0.5 ml of sodium hydroxide 2*N*. The micro-beaker is heated to 80° C approx. (temperature of the solution) on a micro drying block[12].

A freshly prepared solution of 25-35* mg of thionalide in 2-3 ml of acetone is introduced in small drops from a pipette; throughout the addition of the reagent, the solution is stirred vigorously with a short stirring rod (as shown in Fig. 1), particular care being taken that no drop of reagent falls on the sides of the beaker or on the stirring rod. The mixture is cautiously heated to boiling on the drying block, the yellow precipitate allowed to settle and cool for 20-30 minutes. After cooling, the solution is filtered, using low suction, through a porcelain filterstick** (Fig. 2). The beaker, stirring rod, filterstick and precipitate are washed with the mixture containing acetone, water, and ammonium hydroxide (reagent No. 7), in four portions of 2 ml each. In this way the precipitate is freed from both excess thionalide and inorganic ions present during

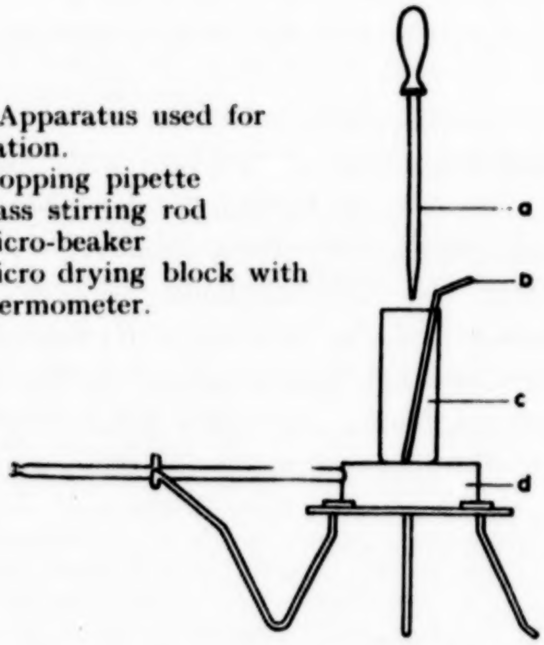


Fig. 1. Apparatus used for precipitation.
a) dropping pipette
b) glass stirring rod
c) micro-beaker
d) micro drying block with thermometer.

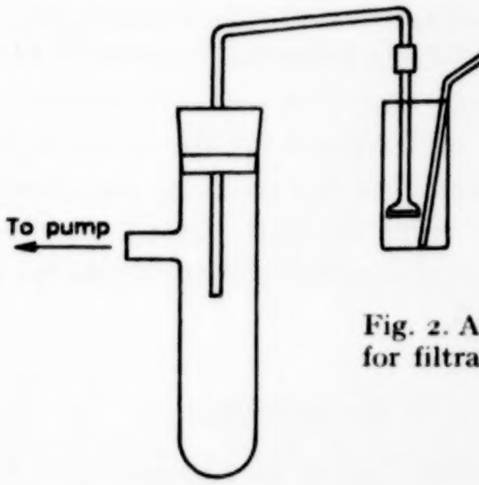


Fig. 2. Apparatus for filtration.

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* 25 mg of thionalide for 3-4 mg thallium; 35 mg of thionalide for 5-6 mg thallium.

** The dimensions of the filterstick used were: overall diameter 11 mm; stem diameter 3-4 mm; overall height 55 mm. All filtersticks used were U.S.A. produce, made by Coors Porcelain Co., Golden.

precipitation. The last portion of wash liquid is collected into a small test tube and examined, on a spot plate for the presence of thionalide as follows:
0.5 ml of the wash liquid is introduced into a depression of a black, glazed porcelain spot plate, one drop of sulphuric acid (1:5) and one drop of iodine solution 0.1*N* are added and the mixture stirred vigorously with a glass rod. In the presence of at least 10 micrograms (γ) of thionalide, a white, floccular precipitate of dithionalide is formed within two minutes; the precipitate is best observed in daylight.

$$2\ C_{10}H_7NHCOCH_2SH + I_2 \rightarrow C_{10}H_7NHCOCH_2\text{-}S\text{-}S\text{-}CH_2CONHC_{10}H_7 + 2\ HI$$

If no thionalide is detected, the filterstick is detached from the suction system and the micro-beaker, containing the precipitate, together with the filterstick and the stirring rod are dried in a preheated drying block of BENEDETTI-PICHLER[13] at 110° C[11] (temperature inside the drying tube; towards that end the temperature of the drying block must be 120° C), using low suction, for 15 minutes; after that period, the drying tube containing the beaker, the filterstick and the stirring rod is taken out of the drying block and cooled outside the block for 15 minutes, without interrupting the suction. After cooling, the beaker together with the filterstick and the stirring rod are removed from the tube, the beaker and the handle of the stirring rod are wiped, as usual, first with a damp flannel cloth and next with two sets of chamois skins, left for 15 minutes on a nickel block near the micro-balance, 5 minutes on a nickel block inside the balance, and finally 5 minutes on the pan of the balance. The beaker, together with the filterstick and the stirring rod, is weighed in the twenty-fifth minute.

The weight of the precipitate, multiplied by the factor 0.4859* gives the amount of thallium in the sample.

The time required for one determination is $2^1/_2$ hours approx. (including preparation of the beaker and the filterstick); two parallel determinations may be carried out in about four hours.

Cleaning of the filterstick, stirring rod and beaker after the determination is effected by washing them alternately with HNO_3-H_2O (1:1) and acetone a few times, and then 2-3 times with bi-distilled water, using portions of 5 ml approx. each time. Drying and weighing of the utensils is carried out as described above under the procedure recommended for the micro-gravimetric determination of thallium.

Table I shows some characteristic results obtained by the above method.

Conclusion

As indicated by Table I, results are exact (maximum relative error ± 0.4%) for 3-6 mg thallium with excess of thionalide between 400% and 800%.

DISCUSSION

1. EMICH's filterstick micro-technique[10] is best suited to this determination:

a) The straight wide necked Emich beaker allows the direct introduction of the reagent into the solution.

b) Adequate stirring is of extreme importance in this determination (see section 4 below). The form of the Emich beaker facilitates efficient stirring.

2. Prior to the precipitation, the sample solution is heated to 80° C. This temperature should not be exceeded, to prevent ejection losses during the subsequent precipitation caused by the ebullition of the acetone of the reagent solution.

3. Precipitation carried out at 80° C approx. gave uniformly good results. BERG's[9] method of precipitation in the cold and subsequent heating did not prove satisfactory under the a.m. conditions.

4. As mentioned in section 1 above, it is advisable to introduce the reagent dropwise into the sample solution, with continuous stirring. In this way, settling out of excess thionalide on the sides of the beaker is avoided. The solution clears and the precipitate settles out properly.

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* The factor given in R. BERG[9a], *loc. cit.* p. 15 is 0.4860. The factor given by the authors, 0.4859, is calculated from the International Atomic Weights of 1952.

TABLE I

MICRO-GRAVIMETRIC DETERMINATION OF THALLIUM WITH THIONALIDE

Exp. No.	*Excess of thionalide* %	*Tl present mg*	*Tl found mg*	*Tl difference mg*	*Relative error* %
1	400	3.000	2.999	−0.001	−0.03
2	400	4.000	4.004	+0.004	+0.1
3	400	5.000	4.986	−0.014	−0.28
4	400	6.000	6.014	+0.014	+0.23
5	500	3.000	2.994	−0.006	−0.2
6	500	4.000	3.992	−0.008	−0.2
7	500	5.000	5.007	+0.007	+0.14
8	500	6.000	5.986	−0.014	−0.23
9	600	3.000	3.012	+0.012	+0.4
10	600	4.000	4.008	+0.008	+0.2
11	600	5.000	5.009	+0.009	+0.18
12	600	6.000	6.016	+0.016	+0.26
13	700	3.000	2.998	−0.002	−0.07
14	700	4.000	4.009	+0.009	+0.22
15	700	5.000	5.018	+0.018	+0.36
16	700	6.000	5.996	−0.004	−0.06
17	800	3.000	3.011	+0.011	+0.37
18	800	4.000	4.012	+0.012	+0.3
19	800	5.000	4.992	−0.008	−0.16
20	800	6.000	6.009	+0.009	+0.15
21	400	2.000	1.967	−0.033	−1.6
22	500	2.000	1.964	−0.036	−1.8
23	600	2.000	1.950	−0.050	−2.5
24	800	2.000	2.028	+0.028	+1.4
25	400	7.000	7.047	+0.047	+0.67
26	400	7.000	7.075	+0.075	+1.07

5. The precipitate is filtered after the solution has cooled to room temperature. Attempts to filter immediately after precipitation invariably gave low results.
6. The wash liquids proposed by BERG[9] (water followed by acetone) were found adequate except when the pH of the distilled water dropped below 7; on those occasions slightly low results were obtained and traces of the dissolved precipitate could be observed as they reprecipitated in the filtrate. Use of a wash liquid composed of either 20 ml acetone, 20 ml water and 3 ml ammonium hydroxide[*,**] conc. or 20 ml acetone, 20 ml water and 1 drop sodium hydroxide solution 2 N[***] (pH 8.5) effectively eliminated this phenomenon; uniformly exact results were obtained forthwith.
7. Experiments proved that the procedure recommended gave exact results whenever a 400%-800% excess of reagent was used, *i.e.* approx. 5.32-9.57 mg for each mg of thallium present. In practice it was found convenient to use 25 mg of thionalide for 3-4 mg of thallium and 35 mg of thionalide for 5-6 mg of thallium.
8. As indicated in Table I, results are exact for amounts of thallium from 3 to 6 mg.

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[*] The ammonium hydroxide must be absolutely pure and must, on no account, leave a silica residue after evaporation. Reliance on the analysis of the reagent, as given on the label, is inadequate; the purity of the ammonium hydroxide must be tested experimentally, as its silica content depends on the quality of the glass in which it has been kept and the duration of its storage[14].

[**] Any ammonium hydroxide left in the precipitate is driven off during the drying period.

[***] The amount of sodium hydroxide involved is negligible and need not be removed by an additional portion of wash liquid.

Experiments carried out on samples containing 2 mg of thallium gave low results (Exp. No. 21-24, Table I); those carried out on samples of 7 mg thallium gave high results (Exp. No. 25-26, Table I). Consequently, 3-6 mg of thallium were chosen as suitable limits for this determination.

SUMMARY

The authors have elaborated an exact micro-gravimetric method for the determination of thallium with thionalide.

RÉSUMÉ

Les auteurs ont élaboré une micro-méthode gravimétrique exacte pour le dosage du thallium au moyen de la thionalide.

ZUSAMMENFASSUNG

Die Verfasser haben eine exakte mikro-gravimetrische Methode zur Bestimmung des Thalliums mit Thionalid ausgearbeitet.

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DETERMINATION OF CARBON IN TITANIUM AND TITANIUM ALLOYS BY COMBUSTION

by

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Carbon is one of the most frequently determined elements in titanium and titanium alloys. The determination of carbon is especially important if carbon electrodes are used in the melting of the titanium. Ordinarily, carbon in titanium and titanium alloys is determined by combustion. In this method the sample is ignited in oxygen and the carbon dioxide is absorbed into a weighed bulb containing Ascarite. A colorimetric method for the determination of carbon in titanium has been proposed, but the method is not applicable to titanium containing more than small amounts of iron or chromium[1]. Also, it is not applicable to the determination of very small amounts of carbon. Considerable difficulty has been encountered with the determination of carbon in titanium and titanium alloys by combustion. SUSS, PANTCHENKO, ARONSON AND SUTTON[2] in their comprehensive report on methods of analysis for titanium issued by Sam Tour and Co. state: "The agreement among laboratories for the combustion method for determining carbon in titanium is not good. Until more analytical work is done, no wholly acceptable method can be presented". STILL, DAUNCEY AND CHIRNSIDE[3] found that low and variable results were obtained for carbon in titanium if the sample were vigorously combusted. Carbon was found to remain in the slag, and carbon dioxide was given off even after 6 hours. These same authors found that if an initial temperature of 1100° C were used, so that the titanium oxidized slowly and did not ignite, good results for carbon in titanium could be obtained. However, the method suffers from the diasadvantage that at least an hour is required for complete burning of the carbon. STILL, DAUNCEY AND CHIRNSIDE found that fluxes including lead and tin were not effective under the conditions they employed.

In view of the above difficulties with the combustion method for determining carbon in titanium, a complete investigation was made of the method. After many trials an accurate and rapid method was developed. It was found that for rapid and complete oxidation of carbon in titanium the following conditions must be met:

(a) Granulated lead must be used as a flux,

(b) An initial temperature of 900° C must be used.

Under these two conditions the titanium will ignite in less than 5 minutes and all the carbon will be driven out of the slag within a few minutes after the ignition. The temperature of the titanium-lead melt, once the ignition starts, rises to about 1600° C as judged by an optical pyrometer. The importance of not using too high an initial temperature cannot be overemphasized. If the initial temperature is high, low and erratic results will be obtained. It is believed by the authors that the low temperature enables the lead to alloy with the titanium before oxidation to lead dioxide takes place. FARRER AND MARGOLIN[4] in a study of the titanium-lead system have shown that lead alloys readily with titanium.

The use of a Vycor or quartz reaction tube with ground glass connections is recommended. This eliminates the necessity of using rubber stoppers or rubber tubing on parts of the apparatus that conduct hot oxygen. Rubber stoppers and rubber tubing can cause very high blanks. The boat that is used to hold the sample is preferably made from ceramic material. Nickel or platinum boats should not be used, since they would alloy with the titanium and lead. The use of alundum to line the bottom of the boat as is done in the determination of carbon in steels to protect the boat, and prevent the iron from melting into globules and occluding unoxidized particles of metal is unnecessary for titanium and titanium alloys. To prevent cracking of the Vycor or quartz reaction tube by the heat that is given off when the titanium ignites, the boat should be insulated in some manner. This is most conveniently done by placing a ceramic cover over the boat and resting the boat on another ceramic cover. Another method of insulating the boat would be to wrap it loosely with asbestos paper that has been previously ignited[5].

The gases from the reaction tube are passed through a "manganese dioxide-copper sulfate-Anhydrone tube" which contains the following reagents: a thick wad of glass wool, manganese dioxide, copper sulfate (on asbestos) and Anhydrone. The purpose of the thick wad of glass wool is to remove particles of lead oxide which are formed. The manganese dioxide removes sulfur dioxide which would be produced, should sulfur be present in the alloy. Only high purity manganese dioxide of large surface area prepared as described by PIGOTT[5] or U.S. STEEL CORPORATION[6] should be used. Such manganese dioxide is available commercially from Fisher Scientific Co. The copper sulfate (on asbestos) serves the purpose of eliminating chlorine. It has previously been used for this purpose by HILLEBRAND, LUNDELL, BRIGHT AND HOFFMAN[7]. The use of copper sulfate is unnecessary except for titanium sponge which sometimes contains a little magnesium chloride. The latter substance enters the sponge as a contaminant when the sponge is manufactured by heating titanium tetrachloride and magnesium metal. Any magnesium chloride contained in the sponge would probably be oxidized in the reaction tube as shown in the following equation[8]:

$$2\ \mathrm{MgCl_2} + \mathrm{O_2} \rightarrow 2\ \mathrm{MgO} + 2\ \mathrm{Cl_2}$$

The purpose of the Anhydrone is to remove water formed by the oxidation of hydrogen in the titanium. The manganese dioxide-copper sulfate-Anhydrone tube should be made of Vycor. If this tube is made of pyrex, it will not be detachable from the reaction tube while the reaction tube is hot, since pyrex has a larger coefficient of expansion than Vycor.

Following the manganese dioxide-copper sulfate-Anhydrone tube is an absorption bulb containing Ascarite and Anhydrone. Absorption bulbs of the closed type are recommended, since open bulbs tend to lose oxygen by diffusion. Following the absorption bulb is a protective tower containing Ascarite and Anhydrone. The protective tower is necessary since air may be sucked back into the reaction tube when the sample ignites. It is necessary to purify the oxygen used in the method by passing it through copper oxide heated to 750° C, and then through Ascarite and Anhydrone. This treatment removes hydrocarbons which are sometimes found in oxygen according to observations in this laboratory.

Coarse drillings, chips or pieces can be used in the method. It may be necessary to pound the drillings with a steel mortar and pestle so the material is compressed and fits into the boat. The use of fine drillings is not recommended, since such drillings are too bulky to fit into the boat. A one gram sample is recommended for the analysis of the usual sample. Five gram samples can be used for samples containing very small amounts of carbon. Attention was given to the possibility of determining carbon and hydrogen by combustion on the same sample. Unfortunately at least a 5 gram sample is required for the accurate determination of hydrogen in commercial titanium and titanium alloys, since the hydrogen content is ordinarily less than 0.02%. If a 5 gram sample is used for the determination of carbon by combustion and the carbon content is fairly high (above 0.2%) low results can be obtained for carbon, since, as has been pointed out by PIGOTT[5], the weight of the absorption bulb may be as much as a few mg lighter than its true weight because of the increase in the temperature of the bulb that results from the sudden absorption of the carbon dioxide. Concerning the possibility of determining carbon and hydrogen on the same sample, it should be pointed out also that at times the hydrogen may be driven out of the titanium without being oxidized. Therefore, the use of hot copper oxide to ensure oxidation of the hydrogen to water is definitely desirable in the determination of hydrogen in titanium[9].

Other fluxes besides lead were not found to be satisfactory for the determination of carbon in titanium and titanium alloys. Among the fluxes tried were tin, copper, and iron.

Apparatus and reagents

A diagram of the apparatus is shown in Fig. 1. The heaters used were of the hinge type (Multiple Unit, Heavy Duti Electric Co., Milwaukee, Wis.)

Ceramic boats, $^{1}/_{2}$ inch in width and $3^{3}/_{4}$ inches long (Leco)
Ceramic covers to fit the above boats (Leco)
Granulated lead, reagent grade (Mallinckrodt or Merck)
Copper oxide, fine wire form, reagent grade
Manganese dioxide, special (Fisher Scientific Co.)
Ascarite
Anhydrone
Carbon tetrachloride, reagent grade
Copper sulfate (on asbestos). Ignite high purity asbestos in a muffle at 1000° C. Mix 3 parts of asbestos with one part of cp anhydrous cupric sulfate by shaking in a bottle. Dry at 150° C for an hour.

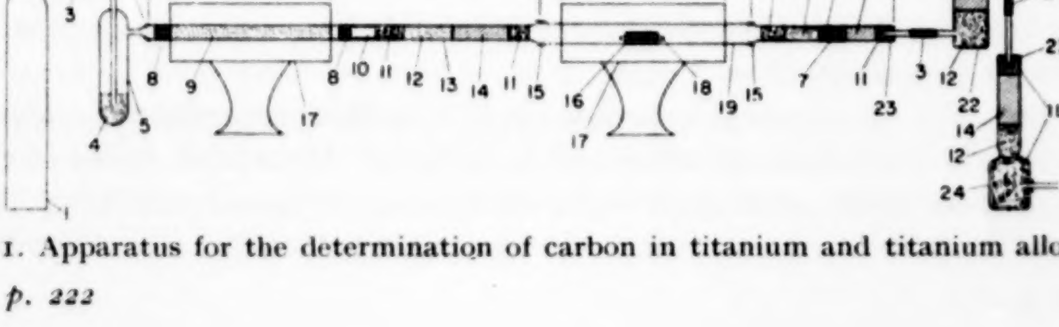

Fig. 1. Apparatus for the determination of carbon in titanium and titanium alloys.

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Key for Fig. 1

1. Tank of oxygen
2. Needle valve
3. Tygon tubing
4. Sulfuric acid
5. Small gas washing bottle
6. Ground glass joint (24/40)
7. Copper sulfate
8. Crumpled ball of fine copper wire
9. Copper oxide
10. Small glass tube inserted to separate copper oxide from Ascarite
11. Glass wool
12. Ascarite
13. Purification tube (Vycor, 25 mm in diameter)
14. Anhydrone
15. Ground glass joint (29/42)
16. Ceramic cover
17. Electric furnace (hinge type)
18. Ceramic boat
19. Reaction tube (Vycor, 25 mm in diameter)
20. Manganese dioxide
21. Manganese dioxide-copper sulfate-Anhydrone tube (Vycor, 17 mm in diameter)
22. Collection bulb
23. Rubber stopper
24. Protective tower

Procedure

Ignite the ceramic boats and covers in a muffle at 1100° C for two hours. Store in a dessicator or an air tight container.

Turn on heaters and heat the copper oxide to 750° C and the reaction tube to 900° C while passing a slow stream of oxygen through the reaction tube. Connect the manganese dioxide-copper sulfate-Anhydrone tube, the absorption bulb and the protective tower. After a few minutes disconnect the absorption bulb and place it in the balance case for 5 minutes. Open it to the atmosphere momentarily to equalize the pressure and weigh, using a similar bulb containing lead shot as a counterpoise.

Weigh out 1 gram of the sample (previously cleaned with carbon tetrachloride and dried thoroughly in an oven at 50° C), and spread the sample over the bottom of a ceramic boat prepared as described previously. Place 2 grams of granulated lead on top of the sample, and place a ceramic cover over the boat. Put the boat on top of another ceramic cover and push the boat and covers into the hottest part of the heater while maintaining a slow flow of oxygen. Connect the manganese dioxide-copper sulfate-Anhydrone tube, the absorption bulb and the protective tower. Increase the flow of oxygen to about 500 ml per minute. The titanium will ignite in about 2 to 5 minutes. Ten minutes after the ignition, disconnect the absorption bulb, allow it to stand 5 minutes in the balance case, open it momentarily to the atmosphere and weigh. The gain in weight is carbon dioxide. Determine the blank by placing lead alone in the boat and carrying the sample through the procedure as above. Calculate the per cent carbon in the sample as follows:

$$\text{Per cent carbon} = \frac{27.29\,(W - B)}{M}$$

where,

W = Wt. of carbon dioxide, grams
B = Wt. of carbon dioxide in blank, grams
M = Wt. of sample, grams

TABLE I

RESULTS FOR CARBON

Sample	*WA 3*	*WA 57*	*WA 67*
% Carbon found	0.276	0.049	0.215
	0.294	0.044	0.213
	0.289	0.047	0.218
	0.278	0.054	0.218
	0.278	0.054	0.205
	0.276	0.049	0.210
	0.292	0.044	0.218
	0.289	0.054	0.213
	0.289	0.049	0.216
	0.276	0.052	0.218
Average % carbon found	0.2837	0.0496	0.2144
Standard deviation (%)	0.0075	0.0039	0.0043

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Results

Table I shows results obtained when three samples were analyzed ten times each by the proposed method.

SUMMARY

Considerable difficulty has been encountered in the past with the determination of carbon in titanium and titanium alloys by combustion. An accurate and rapid method is proposed in this paper. The method depends upon the fact that complete oxidation of carbon in titanium and titanium alloys is obtained if granulated lead is used as a flux at an initial temperature of 900° C. At this temperature the lead alloys with the titanium before oxidation to lead dioxide takes place. Sulfur dioxide and chlorine are eliminated by passing the gases through manganese dioxide and copper sulfate. Purification of oxygen used in the method is necessary.

RÉSUMÉ

De grandes difficultés ont été rencontrées précédemment lors du dosage par combustion du carbone dans un titane ou dans l'un de ses alliages. Une méthode rapide et précise est proposée dans cet article. Une oxydation totale du carbone dans un titane ou dans l'un de ses alliages est obtenue si l'on ajoute du plomb en granules, comme fondant, à une température initiale de 900° C. A cette température le plomb s'allie au titane avant que l'oxydation en dioxyde de plomb se produise. L'anhydride sulfureux et le chlore sont éliminés en faisant passer les gaz à travers du dioxyde de manganèse et du sulfate de cuivre. Une purification de l'oxygène utilisé est nécessaire.

ZUSAMMENFASSUNG

Die Bestimmung von Kohlenstoff in Titan und Titanlegierungen durch Verbrennung machte bisher grosse Schwierigkeiten. Die vorliegende Arbeit enthält nun eine genaue und rasche Methode für diese Bestimmung. Fügt man gekörntes Blei bei einer Anfangstemperatur von 900° als Flussmittel zu, so wird der im Titan oder in der Titanlegierung enthaltene Kohlenstoff vollständig oxydiert. Bei dieser Temperatur legiert sich das Blei mit dem Titan, bevor Oxydation zu Bleioxyd stattfindet. Schwefeldioxyd und Chlor werden entfernt, indem man die Gase durch Mangandioxyd und Kupfersulfat leitet. Eine vorherige Reinigung des verwendeten Sauerstoffes ist erforderlich.

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SUR LA STABILITÉ THERMIQUE DES ÉTALONS ANALYTIQUES. III*

par

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avec la collaboration technique de Mlles COLETTE WADIER et YVETTE SERVIGNE

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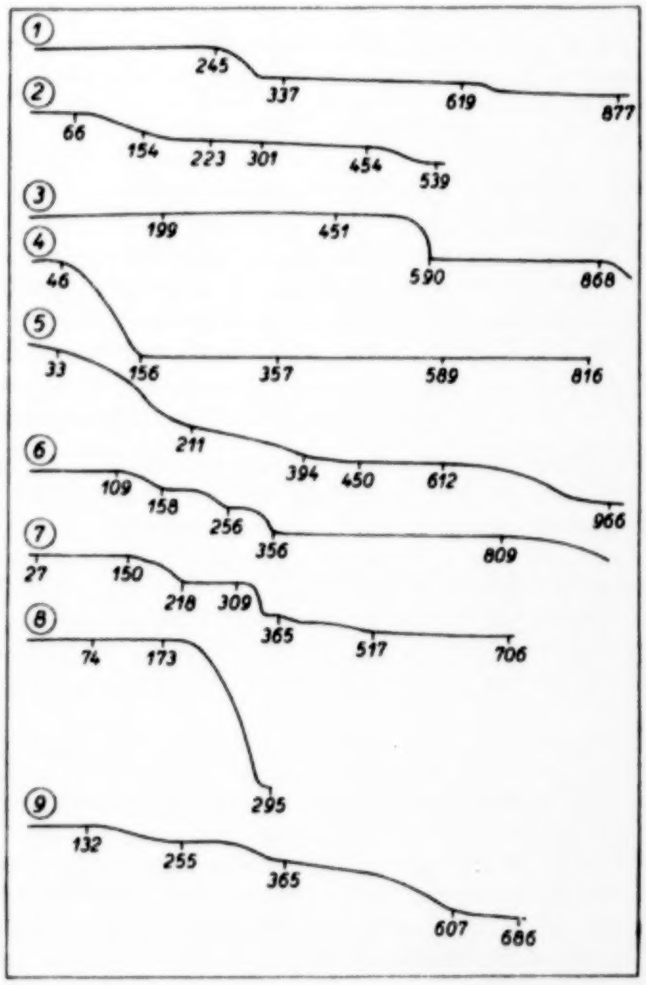
Dans cette troisième série, nous présentons une étude relative aux 12 corps suivants: permanganate de potassium, sulfate de cérium(IV), iodure de potassium, iodate de potassium, bromate de potassium, oxalate de sodium, pyrophosphate de sodium, sulfate d'aluminium, molybdate d'ammonium, citrate de sodium, acide *d*-tartrique et peroxyde de sodium. Ces substances ont été chauffées sur la thermobalance à enregistrement photographique à la vitesse de 300° par heure et avec des poids de substance de l'ordre de 200 mg.



Permanganate de potassium

Ce sel cristallise anhydre et ne retient pas d'eau de mouillage. Sa courbe de thermolyse (Fig. 1) indique qu'il est stable jusqu'à 245°; elle part toujours horizontalement; ce n'est que vers 110° que l'on observe un léger gain de poids. La perte d'oxygène est assez brutale et se manifeste entre 245 et 295°. Alors commence un palier lentement décroissant jusque vers 630°. Entre 245° et 300°, il y a une perte d'environ 1 atome d'oxygène par molécule et la perte globale jusqu'à 700° s'élève à 3 atomes d'oxygène pour 2 molécules de permanganate. Le produit final noir après 700° est assurément un mélange d'oxydes de manganèse et de potassium.

Nous avons observé avec le prisme de sel gemme une bande très forte pour 897 cm^{-1} et une bande faible pour 838 cm^{-1}.

Sulfate de cérium (IV)

Le produit commercial que nous avons eu en mains n'est pas défini mais se comporte comme un mélange de tétrahydrate et de sel anhydre, contenant en moyenne 3.1 H_2O au lieu de 4. Un tel mélange ne conserve son poids que jusqu'à 47°. Il se déshydrate jusqu'à 190-197° (Fig. 2). Le produit anhydre n'est pas stable pendant longtemps et dès 300°, il perd lentement de l'anhydride sulfurique ce qui conduit au produit basique blanc jaunâtre $4SO_3.3CeO_2$. On ne peut donc pas utiliser ce sel directement pour faire une liqueur titrée d'autant plus qu'il est susceptible de renfermer d'autres métaux des terres cériques.

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* Pour le deuxième mémoire de cette série, voir *Anal. Chim. Acta*, 13 (1955) 427.

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Le spectre infrarouge montre naturellement la bande forte relative à l'ion SO_4^{-2} pour 1100 cm^{-1} et 3 bandes plus faibles pour 984, 1002 et 1146 cm^{-1}.

Iodure de potassium

Ce sel est anhydre et conserve un poids constant jusqu'à 715°. Comme on indique son point de fusion à 773°, il est donc déjà légèrement dissocié en fondant. Il est naturellement transparent dans la région du sel gemme.

Iodate de potassium

Ce sel ne perd pas de poids lorsqu'on le chauffe jusqu'à 500° à 150°/heure ou à 300°/heure. Les enregistrements (non reproduits ici) sont des lignes horizontales. Ce sel peut donc être pesé tel quel à la sortie du flacon. Pour l'identification, nous avons préparé les spectres avec un prisme à bromure de césium qui nous a donné une bande faible à 515 et une deuxième assez forte à 374 cm^{-1} et, d'autre part, avec un prisme de sel gemme, nous avons obtenu des bandes à 800 (f), 755 (F) et 738 (TF). Le spectre de la région du bromure de césium a été difficile à préparer et il se montre beaucoup moins net que ceux des chlorates et bromates correspondants.

Bromate de potassium

Ce corps ne change pas de poids jusqu'à 366° où commence nettement sa décomposition. Il peut également se peser directement en le sortant du flacon. Il nous a fourni avec le prisme de bromure de césium, 2 bandes très fortes à 429 et 358 cm^{-1}; avec le prisme de sel gemme, nous avons mesuré deux bandes fortes, l'une à 791 et l'autre à 775 cm^{-1}.

Oxalate de sodium

Ce sel est anhydre et ne retient pas d'eau. Son poids ne change pas jusqu'à 451°. La décomposition s'amorce très lentement et se montre peu sensible jusqu'à 500°; elle s'accélère entre 570 et 590° et s'achève brusquement (Fig. 3) pour faire place au carbonate de sodium éventuellement souillé de charbon provenant, à ces températures, de la dissociation de l'oxyde de carbone. La réaction

$$Na_2C_2O_4 \rightarrow Na_2CO_3 + CO$$

est vérifiée sur le papier photographique avec une précision de 1/75. Le carbonate reste ensuite stable jusqu'à 840° et se dissocie comme nous l'avons dit dans le premier mémoire de cette série.

Le spectre infrarouge de l'oxalate neutre a été préparé avec un prisme de bromure de potassium et un prisme de sel gemme. A côté des deux bandes très fortes 1268 et 1587 cm^{-1} communes à tous les oxalates, nous trouvons deux bandes beaucoup plus faibles à 664 et 762 et une bande très faible à 717 cm^{-1} également commune à la plupart des oxalates simples.

Pyrophosphate de sodium

Le sel commercial contient 10 molécules d'eau (9.96 par le calcul) et sa courbe de thermolyse représentée Fig. 4 indique que ce décahydrate n'est stable que jusqu'à 46°. La déshydratation se poursuit jusqu'à 156°; alors commence le palier horizontal du produit anhydre qui se montre sans changement de poids jusqu'à 826°, limite de notre expérience. En vue de l'établissement d'une liqueur titrée, nous croyons donc préférable de peser le produit anhydre.

Nous avons préparé le spectre infrarouge à plusieurs reprises mais nous n'avons pas pu l'interpréter. Nous relevons avec le prisme de sel gemme, la présence des bandes suivantes: 867 (aF), 918 (F), 995 (F), 1020 (F), 1085 (TF), 1105 (f).

Sulfate d'aluminium

On a donné les températures les plus diverses pour le début de décomposition de ce sel, 200°, 250°, 316°, 450°, etc. Le corps qui nous a servi de point de départ contenait à peu près 16 molécules d'eau. On voit la marche de sa dissociation courbe 5 pour un chauffage de 300°/heure. Le résultat pratique est que pour obtenir une liqueur titrée rigoureuse, il faut maintenir entre 450° et 612° le produit commercial; après quoi, il perd de l'anhydride sulfurique et à 996°, la dissociation est presque terminée.

Le spectre infrarouge tracé entre 6 et 15 μ nous a fourni un nombre de bandes supérieur à celui que l'on peut attendre de cette région, ce qui prouve que l'on a affaire à un complexe, soit 884 (aF), 918 (f), 987 (F), 1075 (TF), 1100 (f).

Paramolybdate d'ammonium

Nous avons utilisé un produit Merck pour analyse de formule 7 $MoO_3 \cdot 3(NH_4)_2O \cdot 4H_2O$. Ce sel est stable; il n'indique aucune perte de poids jusqu'à 109°. Au-delà, comme l'a montré T. DUPUIS (Thèse, Paris, 1954), le sel donne successivement $5MoO_3 \cdot 2(NH_4)_2O$ (de 158 à 208°), puis $4MoO_3 \cdot (NH_4)_2O$ (de 256 à 304°); ensuite, nous obtenons le palier de l'anhydride molybdique de 393° à 751°; après quoi, ce corps se sublime rapidement. La courbe (Fig. 6) nous donne donc la possibilité de faire deux liqueurs titrées au départ de ce sel commercial, soit sous forme de molybdate soit sous forme d'anhydride molybdique.

Le sel de départ est caractérisé par les 5 bandes suivantes: 663 (TF), 836 (aF), 877 (TF), 913 (f), 1420 (F).

Citrate de sodium

Le corps pour analyse de formule $Na_3C_6H_5O_7 \cdot 5^1/_2\ H_2O$ reste stable jusqu'à 145°, après quoi, il perd de l'eau et le palier apparu entre 218° et 309° correspond approximativement à un dihydrate (Fig. 7). Il est impossible d'obtenir le sel anhydre sans décomposition et au-delà de 517°, nous obtenons du carbonate de sodium mélangé de charbon. On peut donc préparer des liqueurs titrées avec ce sel simplement séché à l'air au-dessous de 145°.

Son spectre infrarouge accuse les bandes suivantes: 844 (aF), 895 (aF), 906 (f), 944 (f), 950 (f), 1055 (aF, commune à l'acide citrique), 1075 (aF, commune à l'acide citrique) et 1153 (F) cm^{-1}.

Acide d-tartrique

Chauffé progressivement, il n'accuse pas de variation de poids jusqu'à son point de fusion 170°. La destruction commence insensiblement vers 173° et s'accentue brusquement vers 214° (Fig. 8). On peut donc peser cet acide après l'avoir séché pendant quelques instants à l'état solide.

Le spectre infrarouge dans la région du sel gemme présente les bandes fortes suivantes: 829, 872, 937, 991, 1085, 1128, 1188, 1222 et 1252 cm^{-1}. Les cinq dernières bandes mentionnées sont caractéristiques. Nous les avons déjà interprétées avec J. LECOMTE.

Peroxyde de sodium

Il est impossible d'obtenir des enregistrements reproductibles, tout au moins dans leur partie initiale avec ce corps attendu qu'il capte au cours du chauffage une certaine quantité de gaz carbonique et une quantité non négligeable de vapeur d'eau dont une partie contribue assurément à sa décomposition. Toutefois, on peut dire que d'une manière générale, ce peroxyde commence par gagner du poids au moins jusqu'à 146°; après quoi, entre cette température et 320° en moyenne, il présente un palier horizontal satisfaisant au corps Na_2O_2 éventuellement souillé d'un peu de carbonate de sodium (Fig. 9). Si l'on continue de chauffer, on observe la perte d'oxygène et vers 600° en moyenne, la dissociation se trouve terminée; on arrive à l'oxyde Na_2O (toujours plus ou moins carbonaté). Bien entendu, les oxydes que l'on chauffe en mélange avec l'oxylithe altèrent considérablement la courbe de thermolyse précédente qui résulte d'une moyenne de 4 essais. On peut alors renseigner l'utilisateur sur la valeur du produit qu'il a en mains (réduit en poudre) et pour obtenir un poids déterminé en matière active, il est préférable de s'adresser à un peroxyde ayant été chauffé un quart d'heure vers 250°. Si donc ce corps a été ajouté à la liste ce n'est pas en vue d'en faire une liqueur titrée mais à cause des usages en analyse lorsqu'on doit en prendre un poids déterminé pour faciliter la mise en solution d'un oxyde réfractaire.

Le peroxyde de sodium n'offre pas de spectre dans la région 6-15 μ; les faibles bandes relevées à 868, 881 et 900 cm^{-1} et pas toujours présentes sont dues au carbonate de sodium.

RÉSUMÉ

Dans cette troisième étude de 12 substances utilisées à des titres divers, après pesée, en chimie analytique, nous avons insisté sur le comportement thermique, fourni la température maximum pour le séchage et donné le spectre infrarouge en vue de l'identification rapide des corps et de leurs impuretés éventuelles.

SUMMARY

In this third study of 12 substances used after weighing, in various instances in analytical chemistry, we have laid emphasis on the thermal behaviour and have determined the maximum temperature for drying and the infrared spectrum with regard to the rapid identification of these substances and their possible impurities.

ZUSAMMENFASSUNG

In dieser dritten Untersuchung von 12 Substanzen welche, nach Wägung, verschiedentlich in der analytischen Chemie angewendet werden, wurde der Nachdruck auf das Verhalten beim Erwärmen gelegt; die maximale Trocknungstemperatur und das Infrarotspektrum wurden ermittelt, um eine rasche Identifizierung der Körper und ihrer etwaigen Verunreinigungen zu ermöglichen.

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CHROMATOGRAPHY ON PAPER IMPREGNATED WITH ION EXCHANGE RESINS

PART II. THE SEPARATION OF SELENITE AND TELLURITE*

by

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INTRODUCTION

In a preliminary paper[1] the possibilities of filter paper impregnated with Dowex-50 were discussed and typical applications described. In later work it was found desirable to standardize as far as possible the preparation of the paper. It was then decided to study the separation of Se(IV) — Te(IV) in detail as not many ion exchange studies with these two ions have been recorded[2]. During this study some theoretical aspects of ion exchange paper chromatography were developed.

We shall briefly recall the differences between this technique and ion exchange chromatography on columns. In the latter it is essential that each ion leaves the column and thus must be eluted with a suitable eluant which differs often from that giving the biggest adsorption differences. On paper a substance detected by spraying with suitable reagents may be cut out and ashed; both paper and resin leave practically no residue. Hence the eluant with the biggest adsorption difference can be employed. Swelling of the resin does not have to be taken into account with the paper. On the other hand, development at elevated temperatures is more difficult and up till now the ion exchange paper has not proved satisfactory for development over long distances.

Preparation of the ion exchange paper

One 500 g packet of dry Dowex-50 colloidal aggregates was suspended in $6N$ hydrochloric acid and washed on a funnel with hydrochloric acid solution till the filtrate was free of iron. Then the resin was washed free of acid with distilled water and suspended in a sufficient amount of distilled water to make one liter of suspension. This suspension was shaken for a few minutes before use. To prepare the paper, 50 ml of the suspension were shaken with 50 ml of distilled water, or if the ammonium form was required, with excess aqueous ammonia and poured into a Petri dish. Whatman No. 1 strips or sheets were drawn through this dilute suspension and quickly placed on dry pieces of the same paper to allow uniform drainage.

After drying overnight the paper was visually examined and any part showing accumulation of the resin suspension (usually at the edges) cut off. The paper so prepared is in appearance indistinguishable from untreated filter paper but is more granular to the touch.

The ion exchange capacity was estimated in two ways: (i) measured sections were titrated potentiometrically with $0.01N$ sodium carbonate solution using a Heito pH-meter with glass-calomel electrodes. Pieces 15 cm² large required between 7 and 9.5 ml of the titrant. This corresponds to 4.7-6.3 microequivalents per cm². The average of fifteen determinations being 5.3 meq/cm²; (ii) measured sections were weighed and compared with the weight of untreated paper. The average increase in weight was found to be 0.85 mg/cm². Assuming the value of 5.1 meq/g given by the Dowex Chemical Co., the ion-exchange capacity is 4.3 meq/cm², that is somewhat lower than by titration. The ion exchange properties of the paper may account for this discrepancy.

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* Part I. *Anal. Chim. Acta*, 12 (1955) 142.

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SOME THEORETICAL CONSIDERATIONS

The theory of ion exchange paper chromatography may be approached either from the theory of paper chromatography as worked out by MARTIN AND SYNGE[3] or from the theory of ion exchange columns developed by TOMPKINS AND MAYER[4]. As comparisons both with partition chromatography and ion exchange will be made, the identity of several symbols will be pointed out.

In this work no attempt was made to express the movement of spots in absolute terms and to correlate it with the equilibrium constants, nor to calculate the length necessary for a complete separation of two zones. It was however found possible to establish a simple relation between the R_F value of a spot and the concentration of the eluant, which may permit to determine the valency of an ion as well as the R_F value at a given eluant concentration providing R_F values at other concentrations are known.

According to MARTIN AND SYNGE in the case of partition chromatography

$$R_F = \frac{A_L}{A_L + \alpha A_S} \quad \text{(i)}$$

which may also be written as

$$\frac{1}{R_F} - 1 = \alpha \frac{A_S}{A_L} \quad \text{(ii)}$$

where $R_F = \dfrac{\text{distance travelled by the spot}}{\text{distance travelled by the liquid front}}$; A_L and A_S are the cross sections of the mobile and the stationary phases, and α = partition coefficient = $\dfrac{\text{conc. in stationary phase}}{\text{conc. in mobile phase}}$.

By the way, in ion exchange chromatography α is usually called K_d[4] where

$$K_d = \frac{\dfrac{M_s}{\text{volume of resin}}}{\dfrac{M_e}{\text{volume of solution}}} \quad \text{(iii)}$$

M_s and M_e being the mole fraction of the cation M in the resin and liquid phases.

It has been shown[5] that ion exchange may be formulated according to the law of mass action, thus for an ion M charge x the reaction with the hydrogen form of resin R will be

$$M^{x+} + x\,RH \rightleftharpoons RM + x\,H^+ \quad \text{(iv)}$$

the exchange constant K_e provided the thermodynamic activities are 1, will be

$$K_e = \frac{[\mathrm{RM}]\,[\mathrm{H}^+]^x}{[\mathrm{RH}]^x\,[\mathrm{M}^x]} \quad \dots\dots\dots\dots\dots\dots \quad \text{(v)}$$

or

$$\log K_e = \log \frac{[\mathrm{RM}]}{[\mathrm{M}^x]} + x \log\,[\mathrm{H}^+] - x \log\,[\mathrm{RH}] \quad \dots\dots\dots\dots \quad \text{(vi)}$$

Here log K_e is a constant depending on the reaction (iv) and RH has been assumed constant for chromatographic conditions (very dilute solutions or weak adsorption) by BEUKENKAMP *et al.*[6]. RH has also been shown constant up to about $6 \times 10^{-3} M$ of M^x by TOMPKINS AND MAYER[7]. As will be shown later it should not be constant at low R_F values. However at R_F values below 0.1 the accuracy of the calculations are not sufficient to warrant its consideration.

We have then from (ii) and (iv)

$$\log K_e = \log a + x \log\,[\mathrm{H}^+] - x \log\,[\mathrm{RH}] \quad \dots\dots\dots\dots\dots \quad \text{(vii)}$$

Since only R_F can be measured directly on the paper this must be rewritten as

$$\log K_e = \log \left(\frac{1}{R_F} - 1\right) + \log \frac{A_L}{A_S} + x \log\,[\mathrm{H}^+] - x \log [\mathrm{RH}] \quad \text{(viii)}$$

BATE-SMITH AND WESTALL[8] invented the term $R_M = \log \left(\frac{1}{R_F} - 1\right)$, also in equation (viii) log K_e, log $\frac{A_L}{A_S}$ and x log RH are assumed constant. So we may write

$$x\ \mathrm{pH} = R_M + \text{constant} \quad \dots\dots\dots\dots\dots \quad \text{(ix)}$$

for a given cation being eluted with hydrogen ions.

This relation was obtained while trying to correlate the experimental data of the Se(IV) — Te(IV) separation. To test its validity the elution of La^{+3}, Ni^{+2} and telluryl ions was carried out with various concentrations of sulphuric acid solutions. Fig. 1 shows the pH-R_M graphs and Table I the R_F values measured. Fig. 1 permits

TABLE I

R_F AND R_M VALUES OF LANTHANUM, NICKEL AND TELLURYL IONS IN DIFFERENT CONCENTRATIONS OF SULPHURIC ACID AS SOLVENT

(pH values calculated)

Normality of acid	*pH*	*Lanthanum*		*Nickel*		*Telluryl*	
		R_F	R_M	R_F	R_M	R_F	R_M
0.005	2.3					0.02	1.690
0.01	2.0					0.04	1.380
0.02	1.7					0.10	0.950
0.05	1.3	0.016	1.690			0.21	0.575
0.1	1.0	0.016	1.690	0.04	1.400	0.32	0.327
0.2	0.7					0.46	0.070
0.5	0.3	0.075	1.128	0.30	0.368	0.77	−0.524
1.0	0.0	0.25	0.477	0.57	−0.122		
1.5	−0.17	0.46	0.070	0.72	−0.410		
2.0	−0.30	0.59	−0.158	0.81	−0.631		
3.0	−0.48	0.69	−0.348	0.90	−0.955		

a clear distinction between a mono-, di- or trivalent cation. Also the experimental points seem to justify the assumption that RH, the concentration of the hydrogen form of the resin is constant.

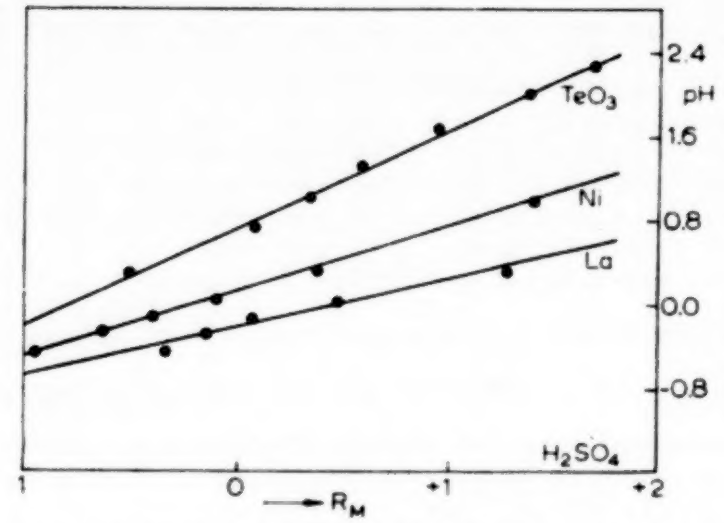

Fig. 1. R_M values of La^{+3}, Ni^{+2} and telluryl ion plotted against pH of eluant (H_2SO_4).

THE SEPARATION SELENITE-TELLURITE

Strips of Dowex-50 paper 30 cm long and 7.5 cm wide were spotted with a mixture of Na_2SeO_3 and Na_2TeO_3 solution containing 1% of each and developed for 20 cm. The paper is then sprayed with a solution of stannous chloride in 5*N* HCl which reduces the two ions to the elements.

The eluants examined were hydrochloric, hydrobromic, perchloric, nitric and sulphuric acids, and also the following organic acids: formic, acetic, citric, lactic and propionic. Tables 2 and 3 show the R_F values of mixtures of selenite and tellurite. Fig. 2, graphs 1-6, show the pH-R_M relationship for each eluant. In all cases the telluryl ion is eluted with the same R_M — pH slope indicating that the ionic species is the same in all cases. The chromatograms with formic and acetic acids are an exception as tellurite precipitates in these two acids and the elution is presumably hindered ~~by~~ this.

TABLE II

R_F VALUES OF SeO_3^{-2} AND TeO_3^{-2} IN DIFFERENT CONCENTRATIONS OF MINERAL ACIDS

(pH values calculated)

Normality of the acids	*0.005*		*0.01*		*0.02*		*0.05*		*0.1*		*0.2*		*0.5*	
pH	*2.3*		*2.0*		*1.7*		*1.3*		*1.0*		*0.7*		*0.3*	
Ion	SeO_3^{-2}	TeO_3^{-2}	SeO_3^{-2}	TeO_3^{-2}	SeO_3^{-2}	TeO_3^{-2}	SeO_3^{-2}	TeO_3^{-2}	SeO_3^{-2}	TeO_3^{-2}	SeO_3^{-2}	TeO_3^{-2}	SeO_3^{-2}	TeO_3^{-2}
HCl	0.82	0.01	0.87	0.02	0.80	0.03	0.81	0.06	0.82	0.16	0.81	0.43	0.80	0.64
HBr	0.82	0.02	0.84	0.08	0.84	0.06	0.84	0.30	0.86	0.32	0.84	0.63	0.85	0.66
HNO_3	0.81	0.03	0.81	0.05	0.82	0.06	0.81	0.13	0.80	0.23	0.80	0.34		
H_2SO_4	0.78	0.02	0.82	0.04	0.81	0.10	0.81	0.21	0.83	0.32	0.81	0.46	0.86	0.77
$HClO_4$	0.83	0.04	0.83	0.02	0.80	0.08	0.82	0.18	0.82	0.26	0.86	0.57	0.85	0.71

TABLE III

R_F VALUES OF SeO_3^{-2} AND TeO_3^{-2} IN DIFFERENT CONCENTRATIONS OF ORGANIC ACIDS (pH values measured)

	Acetic acid			*Citric acid*			*Formic acid*			*Lactic acid*			*Propionic acid*		
Normality	*pH*	SeO_3^{-2}	TeO_3^{-2}	*pH*	SeO_3^{-2}	TeO_3^{-2}	*pH*	SeO_3^{-2}	TeO_3^{-2}	*pH*	SeO_3^{-2}	TeO_3^{-2}	*pH*	SeO_3^{-2}	TeO_3^{-2}
0.005	3.70	0.86	0.01	3.40	0.88	0.02									
0.01	3.60	0.92	0.01	3.20	0.89	0.06	3.15	0.86	0.06						
0.05	3.30	0.94	0.01	2.85	0.85	0.30	2.75	0.79	0.04						
0.1	3.15	0.87	0.01	2.70	0.89	0.39	2.60	0.78	0.05						
0.2	2.95	0.90	0.01	2.50	0.78	0.52	2.50	0.76	0.02						
0.5	2.75	0.86	0.01	2.30	0.87	0.65	2.30	0.78	0.06						
1	2.55	0.88	0.01	2.20	0.84	0.74	2.20	0.77	0.12				2.75	0.81	0.01
2	2.35	0.85	0.04							1.95	0.81	0.62			
4	2.10	0.82	0.09							1.70	0.83	0.74			
6	1.95	0.84	0.09												
8	1.70	0.80	0.04							1.40	0.85	0.85			

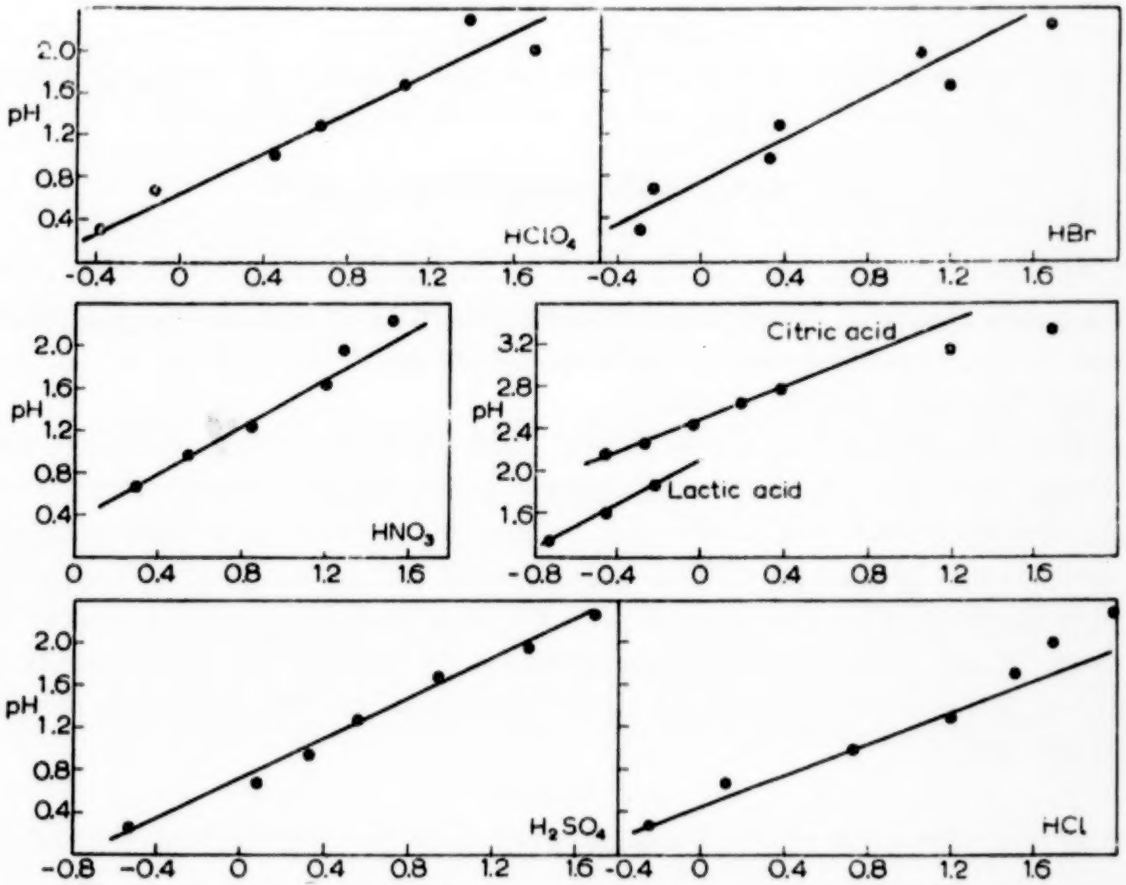

Fig. 2. R_M values of telluryl ions plotted against pH for various eluants.

Selenite behaves identically in all acids and seems to move with an "acid front". It is most likely that the acid in the solvent is somewhat retained by paper and the resin. The selenite advances with this rather than with the pure water preceding it also owing to some adsorption.

We have thus established conditions for a satisfactory separation of selenite from tellurite in a large variety of eluants; also the acidity necessary to elute the tellurite completely if this is required.

It might appear strange that Te(IV) usually known as an anion TeO_3^{-2} exhibits such a cationic character in acid solution. This has been however observed by classical methods[9] as well as by paper chromatography and electrophoresis. At higher concentrations of halogen acids it undergoes complexation forming volatile tetrahalides. Selenite has so far not been observed to exhibit cationic tendencies in dilute acid solution although the ionization constant of selenous acid is much the same as that of tellurous acid[10].

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SUMMARY

The elution of tellurite and selenite on paper impregnated with Dowex-50 was examined with numerous acids. It was possible to relate the R_M value $\left[R_M = \log\left(\frac{1}{R_F} - 1\right)\right]$ with the pH of the eluting acid. This relationship can also be used for the determination of the charge of an ion as was shown with La^{+3} and Ni^{+2} ions.

RÉSUMÉ

L'élution d'un tellurite et d'un sélénite sur papier imprégné de Dowex-50 a été examinée en utilisant de nombreux acides. Il a été possible d'établir une relation entre la valeur de R_M $\left[R_M = \log\left(\frac{1}{R_F} - 1\right)\right]$ et le pH de l'acide utilisé comme éluant. Cette relation peut également servir à la détermination de la charge d'un ion, comme cela a été démontré pour les ions La^{+3} et Ni^{+2}.

ZUSAMMENFASSUNG

Die Elution von Tellurit und Selenit aus mit Dowex-50 imprägniertem Papier wurde mit verschiedenen Säuren studiert. Die Abhängigkeit des R_M-Wertes $\left[R_M = \log\left(\frac{1}{R_F} - 1\right)\right]$ vom pH der eluierenden Säure konnte bestimmt werden. Dieser Ausdruck kann auch dazu dienen, die Ladung eines Ions zu ermitteln, wie für La^{+3} und Ni^{+2} Ionen gezeigt wurde.

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THE LOCATION AND QUANTITATIVE EVALUATION OF VISIBLE AND INVISIBLE CHROMATOGRAPHIC ZONES BY THE R.Rf. IMPEDANCE METHOD

by

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The "Rectified Radio-frequency impedance method" of chromatograph zone location has previously been described[1]. In the conclusion of that paper, the possibility of developing a technique for quantitative measurement was anticipated. Since then, a technique has been worked out by means of which the quantity of solute present in each zone can be estimated. The results of this work are recorded in this paper. Probably the most important feature in connection with the writer's early work was that by introducing the employment of radio-frequencies for chemical analysis it became possible to separate the electrodes from the solution or substance located between them. The use of this "*Condenser-electrode*" principle which he employed in both his early "Q-metric" and "R.Rf." methods has *since become common practice*.

The writer has also applied this principle to zone localization in paper chromatography[5,6]. Since these publications he finds that in Japan YIOHEI HASHIMOTO AND ITSOHIKO MORI too have applied this principle to zone location[4]. Their circuit,

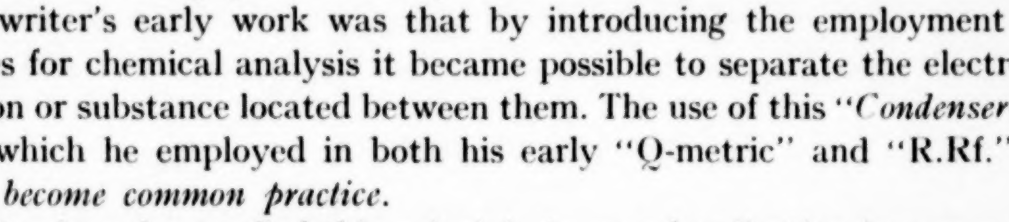

Fig. 1. Diagram of the general set-up required for the operation of Blake's R.Rf. zone localizer. The earthed shieldings of the oscillator, leads, and search gap are not shown.

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like the Hartley Child circuit previously employed by the author in his early Q-metric method of chemical analysis, and the Armstrong "tuned grid — tuned plate" circuit used by Jensen and Parrack[7] obtains its measurements from variations which occur in the valve circuits of the oscillator; whereas the R.Rf. impedance method of zone localization and evaluation[1,5,6],* illustrated in Fig. 1 does not measure either grid or plate current variations but depends on R.Rf. measurements.

Before proceeding further it will be helpful to enumerate some pertinent results that others have obtained by photometric methods.

Photometric achievements

Briefly, the photometric method is as follows[2,3]: After the chromatograph has been "formed" and developed to render the zones visible, dried and then treated with paraffin solution to make it transparent (a preparative process which takes considerable time), a photoelectric cell is passed along the strip, curves are plotted and from these, area measurements are made by means of a planimeter. By comparing these areas against a calibration curve, sugar and other substances have been evaluated successfully.

Relationship between area and solution concentration

It has been shown by photometry[2] that a linear relationship exists between the logs of the concentrations and the areas of the chromatographic zones or spots.

Quantitative photometric evaluations

Estimations have been made also from the size and intensity of the spots[2]. After graphs have been plotted, the areas of those parts of the graph which represent the presence of the solute are measured; they are proportional to the amount of the substance present.

The above photometric results can be reproduced by the R.Rf. impedance method but in a much shorter time, as the zones or spots are neither stained nor rendered transparent. The technique employed is as follows:

G. G. Blake's technique for R.Rf. zone localization and evaluation (*see Fig. 1*)

After "formation" in the usual manner, the chromatograph (at ambient humidity) is passed across the gap which separates the electrodes while radio-frequency current fed from an oscillator (of any stable type) pulses across the gap between them. As each zone crosses the gap, the Rf. current varies in accord with each variation of impedance. The current thus modified is rectified after leaving the second electrode, and the rectified current is measured by means of a zero-shunted micro-ammeter or a mirror galvanometer. The filter paper on which the chromatographs are formed is hydroscopic, therefore, while the meter deflections are practically constant during the short time required for localization *etc.*, by the following day the atmospheric humidity may have changed. In order to make the needful corrections, a control spot or zone containing a known quantity of the solute under investigation is made on a separate strip of paper and measured under the same conditions as the chromatograph. The next day, provided that none of the adjustments on the apparatus have been altered, the meter variations due to changed humidity will be proportional to those previously obtained.

After a chromatograph has been formed it should be dried thoroughly and then hung up for several hours to attain ambient humidity before it is localized.

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* As the apparatus and circuits have been described already in detail[1] no further description is required.

Further investigations by the author

$$R_F \text{ values} = \frac{\text{distance travelled by zone}}{\text{distance travelled by solution front}}$$

The above measurements can be made with additional accuracy by the impedance method as the region of greatest solute density in the zone is indicated with precision by a sharply defined meter deflection.

The shape of zones or spots

The results revealed in Figs. 2 and 3 demonstrate that, provided that each zone or spot contains the same amount of solute after evaporation, the area of the "zone distribution/current graph" (d/c) will be the same irrespective of its shape. Therefore, by employing the R.Rf. zone localizer in conjunction with a planimeter, even a spot which has developed a tail or become distorted, can be estimated quantitatively.

The spots depicted in Fig. 2A all contain the same quantity of $CuCl_2$ delivered from the same pipette, but the shapes of the spots were distorted purposely. Their area measurements are so close that it is obvious that they are in agreement. The

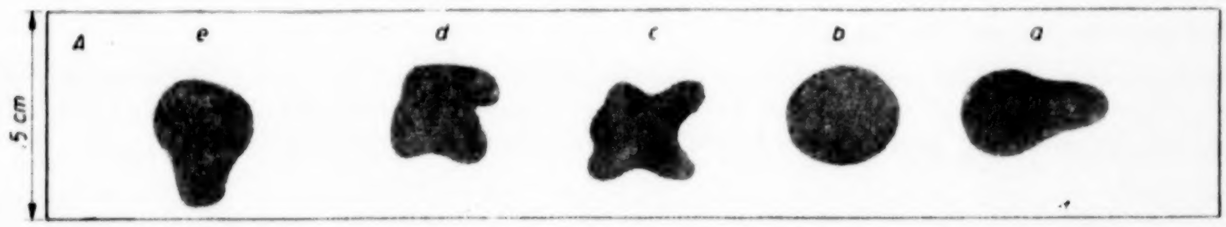
A
e
d
c
b
a
5 cm
A
area = 9.62
9.64
9.65
9.63
9.65
R.Rf. solute distribution/current graphs
B
a
b
e
a
c
b
a
6 cm
B
area = 9.41
9.41
9.42
9.42
9.43
9.43
9.42
R.Rf. solute distribution/current graphs

Fig. 2

A. All the spots on the strip of filter paper contained the same measured quantity of $CuCl_2$. The areas of their "solute distribution/current graphs" are in close agreement.
B. In this figure the spots were delivered by a pipette of slightly smaller capacity.

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same remark applies to the set of spots seen in Fig. 2B, where a slightly differently sized pipette was used.

In Fig. 3 both spots on the filter paper contain the same quantity of $CuCl_2$ solution. Before they were dry, an additional and equal quantity of water was delivered onto the centre of the left-hand spot. Although this enlarged the spot, the area of its d/c graph remained unchanged showing conclusively that these graphs are proportional to the amount of solute which they contain.

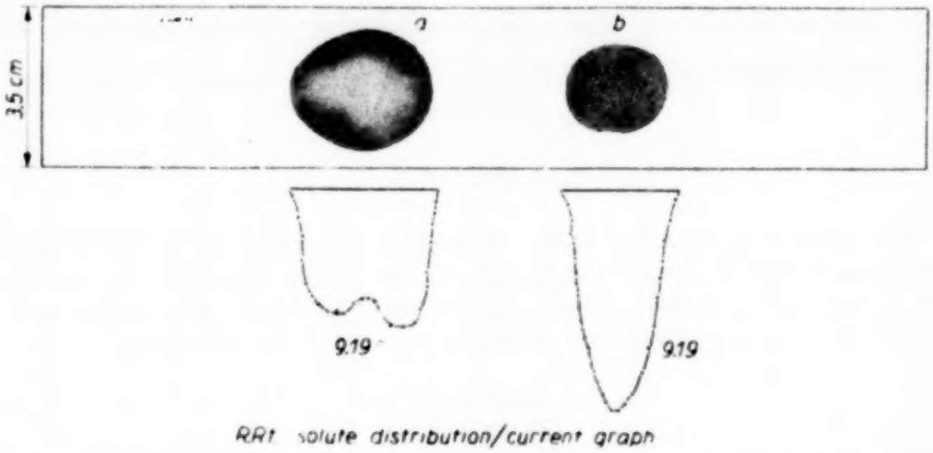

Fig. 3. These two spots each contain an equal amount of solute and although one of them was afterwards enlarged by the addition of distilled water, the areas of their graphs remained unaltered.

d/c graphs for quantitative evaluations

The d/c graphs below the spots in Fig. 2 are the equivalents of similar graphs obtained photometrically but they provide two useful advantages, at any rate in the case of the electrolytes with which the present work was carried out. Invisible zones containing potassium chloride, sodium hyposulphite *etc.*, gave graphs quite as well defined as those obtained for visible zones containing cupric chloride or cobalt chloride.

Many hours which would be required for staining, drying, and for other preparation procedures are thus saved. It is probable also, that many other less conductive or even nonconductive solutes may be localized and evaluated. This extension of the work has not been explored yet; however, even should it be found necessary (after the chromatographs have been formed) to process the papers either to increase the conductivity of the spots or, may be, to render the surrounding paper less conductive, the additional work and time should be well worth while.

Technique for plotting d/c graphs

Before commencing to plot a d/c graph, the chromatograph is first passed across the zone-localizer and by means of a coupling condenser C (Fig. 1), the current is so adjusted that a chosen value is set for the maximum zone deflection thus avoiding the possibility of the current exceeding the range of the micro-ammeter. The d/c graphs are then plotted as the chromatograph is passed across the gap between the electrodes, one of which is fitted with a scale S (Fig. 1), representing that of the micro-ammeter. These plottings are made on a sheet of paper placed on top of the chromatograph. This is passed through the electrodes and drawn across the gap with the latter. Any doubtful reading can be checked by reversing the direction of movement.

A sharply pointed pencil is used for marking the cover paper at convenient intervals. This is inserted through the space separating the electrodes at the points required along its scale. By comparing the areas against a control strip calibrated in suitable fractions of 1 mg/cm², quantitative measurement is obtained.

Negative zero set-back

In cases where the impedances of the various zones vary to such an extent that the range of the meter is insufficient, the latter can be extended to three or four times its normal maximum by suitable zero-shunt adjustment[7].

All other settings remaining unaltered, the last (convenient) meter reading is noted and the needle of the micro-ammeter is then set back to zero. A note is made of the number "X" of micro-amps by which the meter deflection was reduced. This number "X" is added to all the successive readings. Should the end of the scale be reached again, the process is repeated[8].

SUMMARY

In this paper the author applies his R.Rf. Impedance method of chromatograph zone localization to quantitative analysis. Examples are given of "Zone distribution/current graphs" (d/c) which show that quantitative measurement can be made and also that colourless zones or spots can be located and their areas measured without the need for staining.

RÉSUMÉ

Dans cet article, l'auteur applique sa méthode de localisation des zones chromatographiques par mesure d'impédance "R. Rf." à l'analyse quantitative. Des exemples sont donnés montrant que des déterminations quantitatives sont possibles et que des zones ou taches incolores peuvent être localisées et leurs surfaces mesurées sans qu'il soit nécessaire de les révéler.

ZUSAMMENFASSUNG

Der Verfasser beschreibt die Anwendung seiner ,,R.Rf."-Impedanz-Methode zur Lokalisierung der chromatographischen Zonen in der quantitativen Analyse. Es wird gezeigt, dass quantitative Bestimmungen möglich sind und dass auch farblose Ionen und Flecken ohne vorherige Färbung lokalisiert und ihre Oberflächen gemessen werden können.

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COLOR REACTIONS OF ALDEHYDES AND KETONES WITH VANILLIN IN ALKALINE MEDIUM

by

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INTRODUCTION

In an attempt to develop a quantitative method for acetone in biologic material based upon its reaction with vanillin in alkaline medium, we studied, in order to determine specificity, a number of aldehydes and ketones in relation to their reactivity with vanillin.

Salicylaldehyde or 2-hydroxybenzaldehyde is a compound similar in chemical reactivity to vanillin or 3-methoxy-4-hydroxybenzaldehyde. In 1900 FABINYI[1] investigated a reddish-colored complex resulting from the addition of acetone to salicylaldehyde in the presence of 4N sodium hydroxide and demonstrated the formation of the sodium salt of dihydroxybenzalacetone. FROMMER[2] in the same year described a test for acetone in urine, using 10 ml of urine to which was added 1 g of solid potassium hydroxide followed by 8 to 10 drops of a 10% solution of salicylaldehyde in alcohol. The mixture was heated without shaking to about 70° C. In the presence of acetone the zone of contact turned red. LEFFMANN[3] in 1924 reported a similar test for acetone in urine. A red ring forming around the solid sodium hydroxide indicated the presence of acetone. DESHONS[4] in 1926 described a procedure similar to that of FROMMER and LEFFMANN for acetone in spinal fluid. In 1916 CZONKA[5] suggested a clinical method for the determination of acetone based upon its reaction with salicylaldehyde in alkaline medium.

In 1926 BEHRE AND BENEDICT[6] reported a colorimetric method for the determination of the ketone bodies, acetone and diacetic acid, and the ketogenic compound, β-hydroxybutric acid, which on oxidation yields β-ketobutyric acid, more commonly known as acetoacetic acid or diacetic acid. This method involved the condensation of acetone and salicylaldehyde in the presence of concentrated sodium hydroxide with the resulting formation of a yellow to orange color in the reaction mixture. In 1928 BEHRE[7] suggested a semi-quantitative simplification of this method in which the acetone in urine was heated in a test tube plugged at the end with a cotton stopper moistened with salicylaldehyde-alkali reagent. RAVIN[8] in 1936 published a

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criticism of the method of BEHRE AND BENEDICT and suggested modifications to overcome the disadvantages of their technique. In 1940 BEHRE[9] reported improvements in the BEHRE AND BENEDICT method designed to overcome the objections raised by RAVIN.

Vanillin is a compound possessing many chemical properties in common with salicylaldehyde. Both are aromatic aldehydes and both possess a phenol group. Because of their similarity we investigated the potentiality of vanillin as a qualitative and quantitative reagent for carbonyl compounds in general and for acetone in particular. Vanillin possesses several important advantages over salicylaldehyde. The former is a white crystalline compound that can be weighed accurately. It is fairly soluble in water, but not too soluble so that it cannot be purified by crystallization from water. Salicylaldehyde is a liquid, insoluble in water, deteriorating very rapidly and forming a deep brown color on standing even for a short time. It requires purification by distillation for use as a reagent. BEHRE AND BENEDICT found great differences in the delicacy of the color given by different samples of salicylaldehyde reacting with acetone. Furthermore, to be utilized as a reagent for acetone, salicylaldehyde must be dissolved in alcohol. The use of alcohol as a solvent complicates matters, unless the alcohol is purified by means of silver salts and alkali or by dinitrophenylhydrazine to remove carbonyl-containing compounds. Such contaminants also produce colored complexes with salicylaldehyde in an alkaline medium.

Vanillin is more stable, although, according to ENGLIS AND MANCHESTER[10], a dilute solution of vanillin (10 mg per liter in 10% ethyl alcohol) is slowly oxidized to vanillic acid, the oxidation being fairly complete in several weeks. Solutions of vanillin in water do not darken on standing. Fresh solutions, if need be, can be readily and quickly prepared. Concentrated alkali added to salicylaldehyde produces a yellow color at room temperature. The yellow characteristic color produced by acetone and salicylaldehyde with concentrated alkali is necessarily an addition to the color produced by salicylaldehyde and alkali. Vanillin solutions in the cold do not take on color on the addition of 10*N* alkali. Many investigators have utilized vanillin as a reagent in a medium made acid with more or less concentrated solutions of hydrochloric acid or sulfuric acid. Vanillin yields a characteristic yellow color with sulfuric acid without the aid of heat. NIKITIN[11] made a comparison of the reactivity of acetone with vanillin and with salicylaldehyde in equal concentrations of alkali. He found vanillin to be 5.27 times more reactive than salicylaldehyde.

Vanillin was utilized as a test for acetone by ROSENTHALER[12] in 1905 and by KUTSCHEROFF[13] in the same year. The latter employed sulfuric acid as the condensing agent, and the former used hydrochloric acid. FRANCESCONI AND CUSMANO[14] in 1908 reported a test for acetone utilizing an alkaline instead of an acid medium. NIKITIN AND VERSHINSKY[15] in 1937 studied the reaction between vanillin and acetone in a medium made alkaline with a 50% solution of potassium hydroxide. The color developed in their reaction system was green, changing finally to a yellow green color. The color disappeared at the neutral point on the addition of 60% sulfuric acid. On further addition of acid the greenish color reappeared. They did not apply their method to biologic material, and the acetone concentrations they employed were exceedingly high from a biologic standpoint.

EXPERIMENTAL PART

Preliminary tests showed that when acetone was added to an aqueous or alcoholic solution of vanillin in the presence of concentrated sodium hydroxide, a bright yellow to deep orange or red solution developed. The color observed depended upon the quantity of acetone involved. The speed of the reaction was increased, especially with lower concentrations of acetone by warming the reaction mixture in a water bath at about 80° C.

In order to test the specificity of the reaction we studied a number of compounds containing a carbonyl group. For this purpose the vanillin solution was made up to 1% in distilled water and kept in a brown bottle. For ketones we employed as the alkali 40% (10*N*) sodium hydroxide. Because aldehydes readily polymerize in the presence of alkali and often with concomittant color development, we found it advisable to use 20% (5*N*) sodium hydroxide. For some ketones and aldehydes, because of color development with concentrated solutions of alkali alone, we resorted to the use of even more dilute solutions of sodium hydroxide.

The procedure for investigating each compound consisted in adding 1 to 2 mg of the compounds to a test tube followed by 1 ml of vanillin solution and 2 ml of base. A control tube was made up with compound and base, 1 ml of distilled water being substituted for the vanillin solution. Both tubes were immersed in a boiling water bath for ten minutes, unless a strong reaction was observed sooner. Alcohol was used as a solvent for water-insoluble compounds.

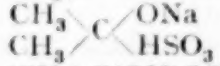
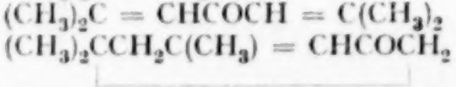
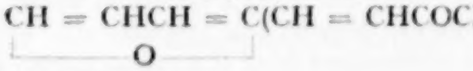
RESULTS

The results of the testing are given in the tables following:

TABLE I

KETONES AND DERIVATIVES THAT YIELD POSITIVE REACTIONS WITH THE VANILLIN-ALKALI REAGENT

A. Straight-chain ketones

Compound	*Formula*
acetone (dimethyl ketone)	CH_3COCH_3
acetone oxime	$CH_3(C = NOH)CH_3$
acetone semicarbazone	$CH_3(C = NNHCONH_2)CH_3$
acetone sodium bisulfite	 $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C<\!\!\begin{matrix}ONa\\HSO_3\end{matrix}$
acetone chloroform	$(CH_3)_2C(OH)CCl_3$
acetol (monohydroxyacetone)	$CH_2(OH)COCH_3$
dihydroxyacetone	$CH_2(OH)COCH_2OH$
acetylacetone	$CH_3COCH_2COCH_3$
acetonylacetone	$CH_3COCH_2CH_2COCH_3$
diacetyl	$CH_3COCOCH_3$
diacetyl monomethyl oxime	$CH_3(C = NOCH_3)COCH_3$
methyl ethyl ketone	$CH_3COCH_2CH_3$
methyl ethyl ketoxime	$CH_3(C = NOH)CH_2CH_3$
diethyl ketone	$CH_3CH_2COCH_2CH_3$
methyl *n*-propyl ketone	$CH_3COCH_2CH_2CH_3$
di-*n*-propyl ketone (P)*	$CH_3CH_2CH_2COCH_2CH_2CH_3$
methyl *iso*propyl ketone (P)*	$CH_3COCH(CH_3)_2$
di-*iso*propyl ketone	$(CH_3)_2CHCOCH(CH_3)_2$
methyl *iso*butyl ketone	$CH_3COCH_2CH(CH_3)_2$
di-*n*-butyl ketone	$CH_3CH_2CH_2CH_2COCH_2CH_2CH_2CH_3$
di-*iso*butyl ketone (P)*	$(CH_3)_2CHCH_2COCHCH_2(CH_3)_2$
methyl *n*-amyl ketone	$CH_3COCH_2CH_2CH_2CH_2CH_3$
methyl *n*-hexyl ketone (P)*	$CH_3COCH_2CH_2CH_2CH_2CH_2CH_3$
methyl *n*-heptyl ketone (T)**	$CH_3COCH_2CH_2CH_2CH_2CH_2CH_2CH_3$
methyl undecylic ketone	$CH_3COCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
ethyl undecylic ketone	$CH_3CH_2COCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
pinacolone	$(CH_3)_3CCOCH_3$
phorone (T)**	$(CH_3)_2C = CHCOCH = C(CH_3)_2$
*iso*phorone (P)*	 $(CH_3)_2\underbrace{CCH_2C(CH_3) = CHCOCH_2}$
furfuralacetone (P)*	 $\underbrace{CH = CHCH = C}_{O}(CH = CHCOCH_3)$

Notes see following page.

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TABLE I (continued)

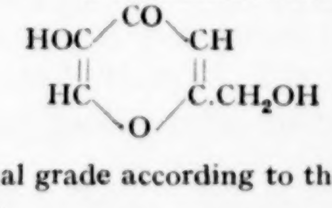
Compound	*Formula*
phenyl acetone (P)*	$C_6H_5CH_2COCH_3$
phenoxyacetone	$C_6H_5OCH_2COCH_3$
benzoylacetone	$C_6H_5COCH_2COCH_3$
benzalacetone	$C_6H_5CH = CHCOCH_3$
di-*m*-nitrobenzalacetone	$(NO_2)C_6H_4CH = CHCOCH = CHC_6H_4(NO_2)$

Diacetyl reacts too violently with 2 ml $5N$ or $10N$ sodium hydroxide. When 0.1 ml of $0.1N$ sodium hydroxide is used together with diacetyl and 1 ml 1% vanillin a deep orange is produced changing to yellow on heating. The control (diacetyl and $0.1N$ sodium hydroxide) gave no color.

B. Alkyl-aryl ketones

Compound	*Formula*
acetophenone	$CH_3COC_6H_5$
acetophenone oxime	$CH_3(C = NOH)C_6H_5$
p-chloracetophenone (P)*	$CH_3COC_6H_4Cl$
m-aminoacetophenone (P)*	$CH_3COC_6H_4NH_2$
p-aminoacetophenone	$CH_3COC_6H_4NH_2$
p-methoxyacetophenone	$CH_3COC_6H_4OCH_3$
p-ethoxyacetophenone	$CH_3COC_6H_4OC_2H_5$
m-nitroacetophenone	$CH_3COC_6H_4NO_2$
2-methyl 5-isopropyl acetophenone	$CH_3COC_6H_3CH_3CH(CH_3)_2$
phenacyl chloride	$CH_3COC_6H_4Cl$
phenacyl bromide	$CH_3COC_6H_4Br$
resacetophenone (2,4-dihydroxyacetophenone)	$CH_3COC_6H_3(OH)_2$
propiophenone (phenyl *n*-propyl ketone)	$CH_3CH_2CH_2COC_6H_5$
p-chlorpropiophenone (P)*	$CH_3CH_2CH_2COC_6H_4Cl$
phenyl *n*-butyl ketone	$CH_3CH_2CH_2CH_2COC_6H_5$
β-napththyl methyl ketone	$CH_3COC_{10}H_7$

C. Cyclic ketones other than those containing a benzene ring

Compound	*Formula*
cyclopentanone	$CH_2CH_2CH_2CH_2CO$
cyclopentanone oxime	$CH_2CH_2CH_2CH_2C = NOH$
cyclohexanone	$CH_2CH_2CH_2CH_2CH_2CO$
cyclohexanone oxime	$CH_2CH_2CH_2CH_2CH_2C = NOH$
alloxan	$NHCONHCOCOCO$
α-hydrindone (1-indanone)	$C_6H_4COCH_2CH_2$
1-ethyl oxindole	$C_6H_4N(C_2H_5)COCH_2$
2,4-diketothiazolidine	$SCONHCOCH_2$
fenchone (T)**	$CH_3CCOC(CH_3)_2CH(CH_2)CH_2CH_2$
kojic acid (5-hydroxy-2-hydroxymethyl 4-pyrone)	

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* (P) indicates that the compound is of practical grade according to the catalogue of Eastman Kodak Company, Rochester, New York, U.S.A.

** (T) indicates that the compound is of technical grade, according to the catalogue of Eastman Kodak Company, Rochester, New York, U.S.A.

TABLE I (continued)

D. Ketone carboxylic acids

Compound	*Formula*
pyruvic acid	$CH_3COCOOH$
acetoacetic ethyl ester	$CH_3COCH_2COOC_2H_5$
acetoaceto-*o*-anisidine	$(CH_3O)C_6H_4NHCOCH_2COCH_3$
triacetoacetic acid	$CH_3COCH_2COCH_2COCH_2COOH$
a-ketopropionic acid	$CH_3COCOOH$
a-ketoglutaric acid	$COOHCOCH_2CH_2COOH$
oxaloacetic acid	$COOHCOCH_2COOH$
levulinic acid	$CH_3COCH_2CH_2COOH$
ethyl levulinate	$CH_3COCH_2CH_2COOC_2H_5$

TABLE II

ALDEHYDES AND DERIVATIVES THAT YIELD POSITIVE REACTIONS WITH THE VANILLIN-ALKALI REAGENT

A. Straight-chain aldehydes

Compound	*Formula*
acetaldehyde	CH_3CHO
paraldehyde	$(CH_3CHO)_3$
propionaldehyde	CH_3CH_2CHO
n-butyraldehyde	$CH_3CH_2CH_2CHO$
n-butyraldoxime	$CH_3CH_2CH_2CH = NOH$
n-butyraldehyde phenylhydrazone	$CH_3CH_2CH_2CH = NNHC_6H_5$
*iso*butyraldehyde	$(CH_3)_2CHCHO$
*iso*valeraldehyde	$(CH_3)_2CHCH_2CHO$
2-ethyl hexaldehyde	$CH_3CH_2CH_2CH_2CH(C_2H_5)CHO$
n-heptaldehyde	$CH_3CH_2CH_2CH_2CH_2CH_2CHO$
n-heptaldoxime	$CH_3CH_2CH_2CH_2CH_2CH_2CH = NOH$
glyceraldehyde	$CH_2OH.CHOH.CHO$

Glyceraldehyde reacts too violently with 1 ml 5*N* or 10*M* sodium hydroxide. With 0.2 ml 5*N* sodium hydroxide glyceraldehyde gives a light yellow color and an orange color with vanillin and the same quantity of alkali.

B. Aromatic aldehydes

Compound	*Formula*
benzaldehyde	C_6H_5CHO
o-chlorbenzaldehyde (P)*	C_6H_4ClCHO
2,3-dimethoxybenzaldehyde (P)*	$(CH_3O)_2C_6H_3CHO$
sodium 4-hydroxybenzaldehyde 3-sulfonate (P)*	$HOC_6H_3(SO_2ONa)CHO$
o-tolualdehyde (P)*	$CH_3C_6H_4CHO$

TABLE III

ALDOLS, KETOLS AND ACETALS THAT YIELD POSITIVE REACTIONS WITH THE VANILLIN-ALKALI REAGENT

Compound	*Formula*
aldol (T)**	$CH_3CH(OH)CH_2CHO$
propionaldol	$CH_3CH_2CH(OH)CH_2CHO$
dimethylacetal	$CH_3CH(OCH_3)_2$
diethylacetal	$CH_3CH(OCH_2CH_3)_2$

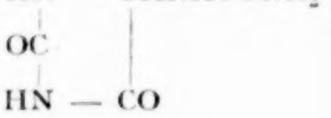
Notes see previous page.

TABLE III (continued)

Compound	*Formula*
glycolaldehyde diethyl acetal	$CH_2(OH)CH(OC_2H_5)_2$
methylal	$H_2C(OCH_3)_2$
ethylal	$H_2C(OCH_2CH_3)_2$
propylal	$H_2C(OCH_2CH_2CH_3)_2$
diacetone alcohol (4-hydroxy-4-methyl-2-pentanone)	$(CH_3)_2C(OH)CH_2COCH_3$

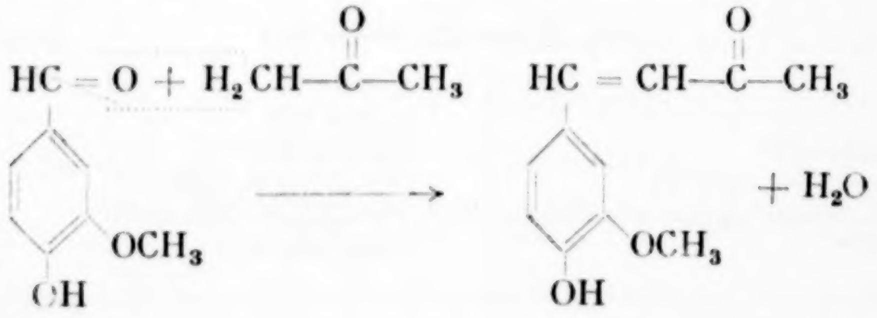
TABLE IV

MISCELLANEOUS COMPOUNDS THAT YIELD POSITIVE REACTIONS WITH THE VANILLIN-ALKALI REAGENT

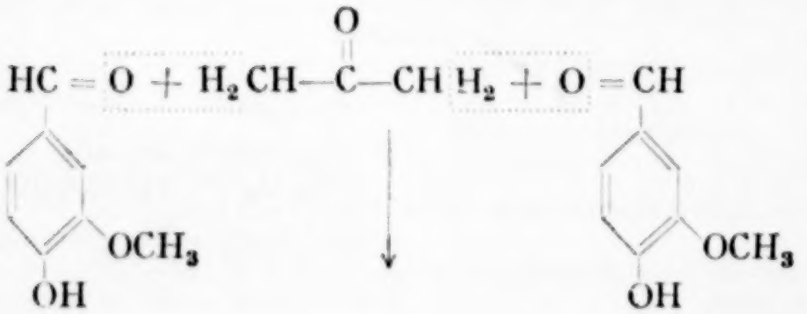
lactic acid	$CH_3CH(OH)COOH$
cysteine	$CH_2(SH)CH(NH_2)COOH$
β-hydroxybutyric acid	$CH_3CH(OH)CH_2COOH$
malic acid	$HOC(COOH)CH(OH)COOH$
maleic acid	$COOHCH = CHCOOH$
citric acid	$HOCCOOH(CH_2COOH)_2$
allantoin	

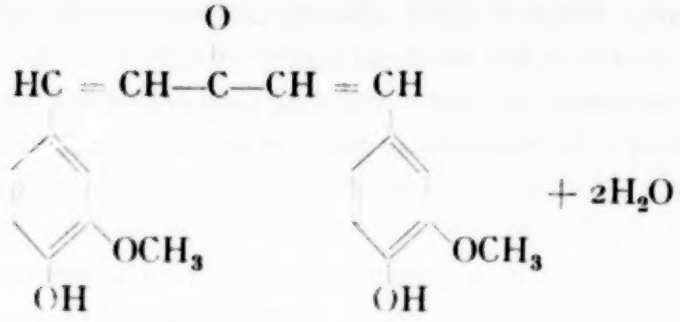
Vanillin has been utilized as a reagent for a great number of organic types. It owes its great and varied reactivity to the fact that it is both a phenol and an aldehyde. It is 4-hydroxy-3-methoxybenzaldehyde. Aldehydes and phenols enter into many organic reactions and exhibit a marked tendency to produce chromogenic condensation products.

Typical overall reactions for vanillin and a ketone are given below:



Vanillin Vanillalacetone





Divanillalacetone

Vanillin in concentrated alkali medium yields a characteristic yellow to orange to red coloration with many compounds with a carbonyl group. The specific color developed and the depth of the color depends upon the nature of the compound or upon the concentration of the compound in the reaction mixture. The reaction is better adapted to ketones than to aldehydes, since the latter tend to resinify in the presence of alkali. The aliphatic aldehydes we have tested react better than aromatic aldehydes. Acetaldehyde yields a good reaction. Benzaldehyde dissolved in alcohol reacts. However, any substituent on the benzene ring, such as a halogen atom, a hydroxy, methoxy, nitro or amino group produces a doubtful test because color development occurs with alkali alone. Such is the case with *p*-hydroxybenzaldehyde, 2,4- and 3,4-dichlorbenzaldehyde, *o*- and *m*-nitrobenzaldehyde, 2,4-dihydroxybenzaldehyde, 3,4-diethoxybenzaldehyde, hydroxy-5-chlorbenzaldehyde, and 2-hydroxy-3-methoxybenzaldehyde. Formaldehyde and formic acid do not react.

Aldehydes have been reported to interact with vanillin in a sulfuric acid medium. Pougnet[18] in 1909 reported a test for formaldehyde in the presence of concentrated sulfuric acid. A yellowish-green color was produced, turning red on heating. Angelico[19] in 1910 demonstrated that aqueous solutions of various aldehydes with vanillin and concentrated sulfuric acid produced fuchsin red colorations.

Color reactions for ketones with vanillin have been reported by Rosenthaler[12] in 1905. He performed experiments with a few ketones, acetone diethyl ketone, dipropyl ketone, methyl ethyl ketone, methyl propyl ketone, methyl butyl ketone, acetylacetone, acetonyl acetone, benzalacetone, pinacolone. With the liquid ketones he used two drops and with the solid ketones, small crystals in one percent vanillin in hydrochloric acid. He allowed the reaction mixtures to stand at room temperature for 15 minutes, noted the reaction, and then applied heat. With acetone he obtained at room temperature an immediate light rose red changing to a bright green. The reaction with acetone was very sensitive. On heating the color showed a light green in direct light and red in transmitted light, finally changing to violet. With diethyl and dipropyl ketone he observed a rose red, which turned green on heating. With methyl ketone, methyl propyl ketone and ethyl butyl ketone no coloration was produced at room temperature. On heating, however, a green color was first produced with methyl ethyl ketone, changing to blue, and with methyl propyl ketone and methyl butyl ketone, green finally changing to blue green.

Acetylacetone, according to Rosenthaler[12], at room temperature gave a rose red color changing to green. On heating the reaction mixture revealed in direct light a green, and in transmitted light a red color changing to green. Acetonylacetone gave a red color only when heated. Benzalacetone yielded a rose red color at room temperature and a red color on heating.

The ketones we investigated show varying degrees of reactivity in alkaline medium. Ketones with one of the radicals a methyl group react readily. When both alkyl radicals are methyl groups, such as dimethyl ketone or acetone, the reactivity is at its maximum.

When one alkyl radical is a methyl group and the other a higher analogue, the reactivity is somewhat lessened. Thus, methyl ethyl ketone, $CH_3COCH_2CH_3$, is less reactive than dimethyl ketone or acetone, CH_3COCH_3. Further lengthening of the carbon chain in one of the radicals, as in methyl propyl ketone, reduces the reactivity to a still greater degree. Such compound as methyl propyl ketone, $CH_3COCH_2CH_2CH_3$, is less reactive than methyl ethyl ketone, $CH_3COCH_2CH_3$. Such compound as methyl undecylic ketone, $CH_3CO(CH_2)_{10}CH_3$, is considerably less reactive.

Ketones with no methyl group react less intensely than ketones in which one radical is a methyl group. Diethyl ketone is less reactive than dimethyl ketone and less reactive than methyl ethyl ketone. Diethyl ketone is again less reactive than di-*n*-propyl ketone. Finally such compounds as 9-heptadecanone, $CH_3(CH_2)_7CO(CH_2)_7CH_3$ and 10-nonadecanone, $CH_3(CH_2)_8CO(CH_2)_8CH_3$, exhibit no reactivity.

The presence of an aryl group also diminishes the reactivity. Acetophenone, $CH_3COC_6H_5$, is less reactive than ketones with both radicals of the aliphatic type. Phenacyl chloride, $C_6H_5COCH_2Cl$, phenacyl bromide, $C_6H_5COCH_2Br$, phenoxyacetone, $C_6H_5OCH_2COCH_3$, phenyl acetone, $C_6H_5CH_2COCH_3$, *p*-hexylacetophenone, $CH_3(CH_2)_4CH_2C_6H_4COCH_3$, phenyl *n*-propyl ketone, $C_6H_5COCH_2CH_2CH_3$, phenyl *n*-butyl ketone, $C_6H_5COCH_2CH_2CH_2CH_3$, and benzalacetone, $C_6H_5CH = CHCOCH_3$, react less intensely than ketones with aliphatic groups. Methyl undecylic ketone, $CH_3CO(CH_2)_{10}CH_3$, reacts slightly, but phenyl undecylic ketone, $C_6H_5CO(CH_2)_{10}CH_3$, not at all.

When both radicals in the ketone molecule are aryl groups, reactivity disappears altogether. Benzophenone, $C_6H_5COC_6H_5$, phenyl *p*-tolyl ketone, $C_6H_5COC_6H_4CH_3$, and di-*p*-tolyl ketone, $CH_3C_6H_4COC_6H_4CH_3$, do not react. Benzalacetone, $C_6H_5CH = CHCOCH_3$, and benzalacetophenone, $C_6H_5CH = CHCOC_6H_5$, react very slightly, but dibenzalacetone, $C_6H_5CH = CHCOCH = CHC_6H_5$, proved negative.

Benzoylacetone, acetophenone, ethyl phenyl ketone, benzophenone, benzoin, and benzil were reported by ROSENTHALER[12] in 1905 to give no reactions, when vanillin and these compounds react in a hydrochloric acid medium. We have observed that water-insoluble compounds may give a positive reaction when they are first dissolved in alcohol. In 1953, however, ROSENTHALER AND VEGEZZI[20] reported positive color reactions with acetophenone, benzophenone, benzalacetone and benzylidineacetone. They used sulfuric acid as the medium for the interaction. Sulfuric acid is known to be more reactive than hydrochloric acid and to react with a great variety of organic compounds. We have chosen an alkaline medium for our vanillin reagent to limit its reactivity.

The ketonic acids, pyruvic acid, levulinic acid, diacetic acid, triacetic acid, α-ketopropionic acid, α-ketoglutaric acid, and oxaloacetic acid, give positive reactions.

The cyclic ketones, cyclopentanone and cyclohexanone, react very vigorously. In concentrations as low as 0.5 γ, cyclopentanone quickly produces a yellow reaction mixture, rapidly changing to orange and finally to deep cherry red.

Among miscellaneous compounds yielding a positive reaction with vanillin in alkaline medium we found cysteine and the following hydroxy acids: glycolic acid, lactic acid, β-hydroxybutyric acid, malic acid, maleic acid, citric acid, and kojic acid. Allantoin and alloxan also gave positive reactions. With glycolic acid, malic acid and maleic acid best results are obtained when 1 ml of 5*N* sodium hydroxide instead of 2 ml of 10*N* alkali are used.

SUMMARY

Vanillin in alkaline medium is a very useful reagent for the detection of carbonyl-bearing compounds, especially ketones, yielding yellow, orange or red colorations in the reaction mixture. The intensity of the reaction and the particular color produced depends upon the constitution of the compound and its concentration. The reaction works best with aliphatic ketones, especially when these contain a methyl group. Acetone with two methyl radicals yields the maximal color. As the carbon chains in the ketone radicals lengthen, reactivity diminishes. Aromatic ketones are least reactive or do not react at all.

RÉSUMÉ

La vanilline, en milieu alcalin, constitue un réactif très avantageux pour l'identification des composés renfermant un groupe carbonyle, en particulier les cétones, en donnant des colorations jaune, orange ou rouge. L'intensité de la réaction et la couleur particulière obtenue dépendent de la constitution du composé et de sa concentration. C'est avec les cétones aliphatiques, et spécialement lorsqu'elles renferment un groupe méthyle, que cette réaction est la plus nette. L'acétone avec ses deux radicaux méthyle donne la coloration maximum. La réactivité diminue au fur et à mesure que s'allonge la chaîne d'atomes de carbone des radicaux des cétones. Les cétones aromatiques réagissent le moins facilement ou même ne réagissent plus du tout.

ZUSAMMENFASSUNG

Vanillin, in alkalischem Medium, hat sich zum Nachweis von Verbindungen mit einer Carbonylgruppe, besonders Ketonen, vorzüglich bewährt indem es eine gelbe, orange oder rote Farbe liefert. Die Intensität der Reaktion und die in jedem besonderen Falle erhaltene Farbe ist von der chemischen Zusammensetzung und Konzentration der Verbindung abhängig. Das beste Resultat wird mit aliphatischen Ketonen erzielt, besonders wenn sie eine Methylgruppe enthalten. Das Aceton mit seinen zwei Methylradikalen gibt die stärkste Farbe. Die Reaktivität nimmt ab wenn die Kohlenstoffkette im Ketonradikal an Länge zunimmt. Aromatische Ketone reagieren am schlechtesten oder überhaupt nicht.

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A FLUORIMETRIC DETERMINATION OF TIN

by

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INTRODUCTION

In the analysis of nonferrous metallurgical materials it is customary to separate small amounts of tin as metastannic acid by digestion with nitric acid, provided the material is soluble in nitric acid. However, the precipitate is subject to contamination by a number of elements, such as iron, copper, zinc, arsenic, antimony, phosphorus, vanadium, tungsten, silicon, niobium and tantalum[1]. The purification of the precipitate by fusion with sodium carbonate and sulphur is unsatisfactory, in that the fusion must be repeated and complete separation of tin is doubtful. For this reason the precipitation of tin by digestion with nitric acid can only be regarded as a preliminary separation. A definite need exists therefore for a method which would permit the determination of the true tin content in the impure metastannic acid precipitate.

A fluorimetric method for the detection of stannous ions on paper was reported[2], using as reagent the ammonium salt of 6-nitro-2-naphthylamine-8-sulphonic acid. The reagent gave a blue fluorescence with stannous ions which increased in intensity when the spot was exposed to ammonia fumes. It was claimed that this reaction was specific for stannous ions among 47 ions examined.

This method appeared to offer a useful approach, provided the conditions for the quantitative estimation of small amounts of tin in solution could be established.

EXPERIMENTAL

Apparatus

Measurements were made with a Hilger Uvispek Photoelectric Photometer H 700/302 in conjunction with the H 730 Fluorescent Attachment using an H. 556.001 Woods Glass Filter-Chance No. OXI to isolate the exciting radiation of 3650 Å. The cells had a capacity of approximately 18 ml and were provided with black glass lids. The incident radiation passed upwards through the base of the cells. A set of two yellow filters supplied in one circular mount was inserted between the cell containing the fluorescent solution and the photocell compartment in order to absorb the exciting radiation, but to transmit the fluorescent radiation. They were:
H. 730.004 Yellow Filter-Chance No. UY. 18 and
H. 730.005 Pale Yellow Gelatine Filters-Wratten No. 2 A.

The fluorescence was measured by plotting a calibration curve, using fluorescing standards which contained known amounts of tin. The strongest fluorescing standard of a series was taken to give a reading of 100% transmission on the spectrophotometer scale.

Reagents

Standard tin solution. Dissolve 1.0000 g A.R. tin in 5*N* HCl and make up with 5*N* HCl to 1000 ml
1.00 ml = 1.000 mg tin.

Mercuric chloride solution. Prepare a saturated solution of A.R. mercuric chloride in cold water

$5N$ *Ammonia solution.* Dissolve 1 g ammonium hypophosphite B.D.H. in 100 ml $5N$ ammonia.
Hypophosphorous acid B.P.C. 30%.
Preparation of the ammonium salt of 6-nitro-2-naphthylamine-8-sulphonic acid[3]. 2-Aminonaphthalene-8-sulphonic acid (33.0 g) was dissolved in concentrated H_2SO_4 (450 ml) by adding it gradually in small portions and stirring. When solution was complete, urea (12.9 g) was dissolved in the mixture to prevent the formation of nitrous acid during the nitration. The solution was now chilled to —20° C by using an ice-salt external cooling bath and adding dry ice directly into the solution. The nitrating acid, consisting of a mixture of 11.6 ml HNO_3 (S.G. 1.42) and 18.0 ml H_2SO_4 (S.G. 1.84) was then added from a dropping funnel over a period of two hours using slow mechanical stirring and keeping the temperature at $-20°$ C. The brown nitration mixture was left at $-20°$ C for another hour and then poured onto crushed ice (1000 g).

A pale yellow precipitate formed immediately which was filtered after one hour standing and washed with icewater to remove excess sulphuric acid. The precipitate was macerated with $15N$ NH_4OH until just alkaline and was placed in the refrigerator to cool. A deep red ammonium salt immediately precipitated out in lustrous plates. The salt was recrystallized from hot water in presence of animal charcoal. The yield of the crude ammonium salt is 40.1 g which corresponds to 95% theoretical.
Preparation of reagent. Dissolve 0.1 g of the ammonium salt of 6-nitro-2-naphthylamine-8-sulphonic acid in 100 ml boiled water.

The original experiments on the fluorimetric detection of the stannous ions were carried out on paper. It was therefore necessary to study the conditions under which fluorescence was developed in solution. For this initial qualitative work an ultraviolet lamp was used which permitted visual observation of fluorescence.

When an aqueous solution of the reagent was added to an acid solution of stannous chloride, the colour of the solution changed to orange due to the colour of the reagent itself but only very faint fluorescence was observed. When the solution was made alkaline with ammonia a strong blue fluorescence developed and the solution became turbid due to the precipitation of the tin. If sodium hydroxide was used in place of ammonia the initial precipitate redissolved but the fluorescence was almost completely quenched.

Complexing agents

It therefore became necessary to find a suitable complexing agent which would keep the tin in solution under slightly alkaline conditions, without reducing appreciably the intensity of the fluorescence. Several complexing agents were tried, *viz.* diammonium hydrogenphosphate, ammonium bifluoride, citric acid and tartaric acid.

To an acid solution of stannous chloride the complexing agent was added, then the reagent in aqueous solution and ammonia added till the solution was alkaline. The solution was observed for freedom from precipitation and intensity of fluorescence.

It was found that all complexing agents except ammonium bifluoride were capable of keeping the tin in solution under slightly alkaline conditions. In the presence of ammonium phosphate the fluorescence of the solution was less intense than when citric acid or tartaric acid were used. Tartaric acid was preferred to citric acid because less was required to keep the tin in solution.

Reducing agents

The authors of the spot test for stannous ions[2] recommended hypophosphorous acid as the reducing agent. While hypophosphorous acid was quite effective in reducing stannic ions on paper, it worked only very slowly in aqueous solution unless mercuric ions were present as catalyst. This reaction has been reported by EVANS[4], who employed it for the reduction of tin prior to titration with iodine. Since very small amounts of mercury salts were effective in catalytically accelerating the reduction to stannous ions, FEIGL[5] developed a spot test for mercury based on this reaction. Hypophosphorous acid in presence of small amounts of mercuric chloride was found to be a very effective reducing agent for tin without affecting the reagent itself.

Other reducing agents which were tried and found ineffective were hydroxylamine, hydrazine sulphate, and sodium metabisulphite ($Na_2S_2O_5$). Sodium hyposulphite ($Na_2S_2O_4.2H_2O$) on the other hand was such a strong reducing agent that it reduced the reagent itself, producing a brilliant blue fluorescence.

Some metallic reducing agents also reduced the reagent to varying degrees. Nickel caused very faint fluorescence, while aluminium, zinc, lead and antimony caused slight fluorescence. Iron on the other hand reduced the reagent to a considerable extent, producing strong fluorescence.

Development of fluorescence

Since stannous tin readily undergoes aerial oxidation to stannic tin it was considered essential to perform the reduction of the tin as well as the development of fluorescence in an inert atmosphere of carbon dioxide.

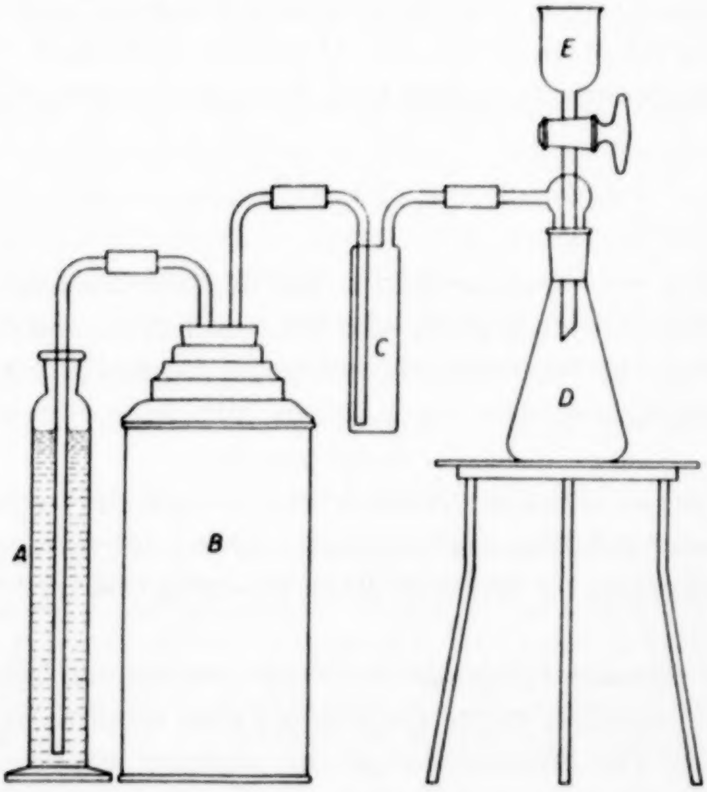

Fig. 1.

Apparatus

For this purpose the small apparatus shown in Fig. 1 was employed. It consisted of a 150 ml Erlenmeyer flask (D) with a B 19 Quickfit neck into which fitted a small funnel (E) with a sidearm to allow CO_2 being passed into the flask. The CO_2 was generated from dry ice in a thermos flask (B). The gas pressure was adjusted by a pressure regulator valve (A), consisting of a glass cylinder with a constricted neck which was filled with water to about 5 cm from the top. A piece of glass tubing reaching almost to the bottom of the cylinder was connected to the thermos flask by means of a well fitting rubber stopper. This pressure regulator valve has been devised by the microanalyst of this university[6]. It has been used for several years for the Dumas micro nitrogen determinations. The advantage of this regulator over the more conventional type using mercury lies in its simplicity and ease of assembly. Furthermore, no health hazard is involved as the escaping gas passes through water. This obviates the carry-over of poisonous mercury vapours which occurs in the usual type of regulator. The CO_2 from the thermos flask passed through an empty bubble counter (C) which was connected to the sidearm of the funnel.

Procedure

10 ml of a standard tin solution containing 1.000 mg Sn/ml in 5*N* HCl were measured accurately in the 150 ml Erlenmeyer flask, 1 g tartaric acid added, the Quickfit funnel fitted and CO_2 passed to displace the air from the apparatus. The solution was heated to boiling and then left to cool and 1 ml of mercuric chloride solution added by means of a 1 ml pipette, followed by 1 ml of hypophosphorous acid. The tip of the pipette was inserted directly into the flask by lifting the funnel slightly. This prevented precipitation occurring in the funnel. The solution was boiled gently for about 10 minutes until the black precipitate which first formed coagulated and the solution cleared. 30 ml 5*N* NH_4OH were added, the solution cooled to room temperature and 10 ml of the reagent added. All these operations were performed while CO_2 was passing through the apparatus. The orange coloured solution showed a strong blue fluorescence under ultraviolet light. A blank run with all the reagents but without tin was completely free of fluorescence.

Having established the conditions under which fluorescence was developed in solution, it was still necessary to study the effect of such variables as pH, time of standing, concentration of the reagent and concentration of tin.

Effect of pH

A fluorescent solution was prepared using 10 ml of a standard tin solution containing 1.000 mg Sn/ml in 5*N* HCl as described under development of fluorescence. The fluorescent solution was left to stand for 2 hours under CO_2 to attain maximum fluorescence. This solution was then made up to 1000 ml in a volumetric flask.

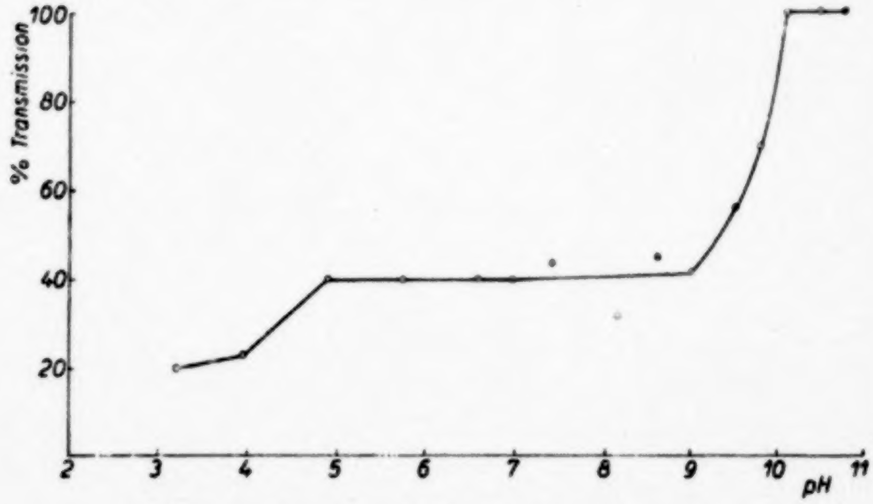

Fig. 2. The effect of pH on fluorescence.

A series of 12 solutions was prepared by transferring 10 ml aliquots of the fluorescent solution to 100 ml volumetric flasks. To each flask was added ammonia or tartaric acid to give a pH range from 3.2 to 10.8. The solutions were then made up to 100 ml. The pH was measured with a laboratory model Cambridge pH meter. Under these conditions maximum fluorescence was found at a pH of 10.2 to 10.8 (Fig. 2). This experiment was repeated in the pH range of 9.5 to 10.8 and strongest fluorescence was found at a pH of 10.5 to 10.8. This corresponds to an excess of 6 to 15 ml 5*N* NH_4OH in 100 ml. All solutions prepared for the following experiments contain an excess of 10 ml 5*N* NH_4OH per 100 ml.

Time of standing

It had been observed previously that the fluorescence did not attain its maximum intensity immediately after the addition of the reagent. The change of intensity with time was therefore investigated.

Fluorescent solutions were prepared as described under development of fluorescence, using 10 ml of the standard tin solution containing 1.000 mg Sn/ml. The reagent was added to the cold solutions and the mixtures were then left to stand for varying periods of time before making up to 1000 ml with distilled water. 10 ml of these fluorescent solutions were then transferred into 100 ml flasks, 10 ml $5N$ NH_4OH added and the solutions made up to volume.

Table I records the changes of intensity of fluorescence (measured as percentage transmission on the spectrophotometer scale) against the time of standing for one series of experiments:

TABLE I

Time of standing (min)	10	30	60	90	120	180	overnight
Transmission (%)	42	58	83	97	93	100	80

It is evident, that the solutions should be allowed to stand for at least 90 minutes after the addition of the reagent. The adopted standard procedure is, to allow to stand for two hours to attain maximum fluorescence. Standing overnight causes the fluorescence to decrease.

It had been noticed, that a shorter standing time was required when the reagent was added to the hot solution, or when the mixture was heated. However, it was found that under these conditions the blank alone would sometimes produce a faint fluorescence and it was considered safer to develop the fluorescence at room temperature, even if it required 1½ to 2 hours standing.

Concentration of the reagent

A series of 4 solutions was prepared as under development of fluorescence, using 10 ml of standard tin solution containing 1.000 mg Sn/ml. To these solutions varying amounts of a 0.1% solution of the reagent were added and left to stand for 2 hours. The solutions were then made up to 1000 ml. 10 ml of these solutions were transferred into 100 ml volumetric flasks, 10 ml $5N$ NH_4OH added and made up to volume. Table II records the intensity of fluorescence (measured as percentage transmission on the spectrophotometer scale) against the concentration of the reagent.

TABLE II

Volume of 0.1% reagent (ml)	4	6	8	10
Transmission (%)	69	80	100	100

While 8 ml of a 0.1% solution of the reagent are sufficient, it was decided to use 10 ml for 10 mg tin.

Concentration of tin

The next step was to establish the range where the intensity of the fluorescence is a linear function of the tin concentration. For this purpose a fluorescent tin solution was prepared as

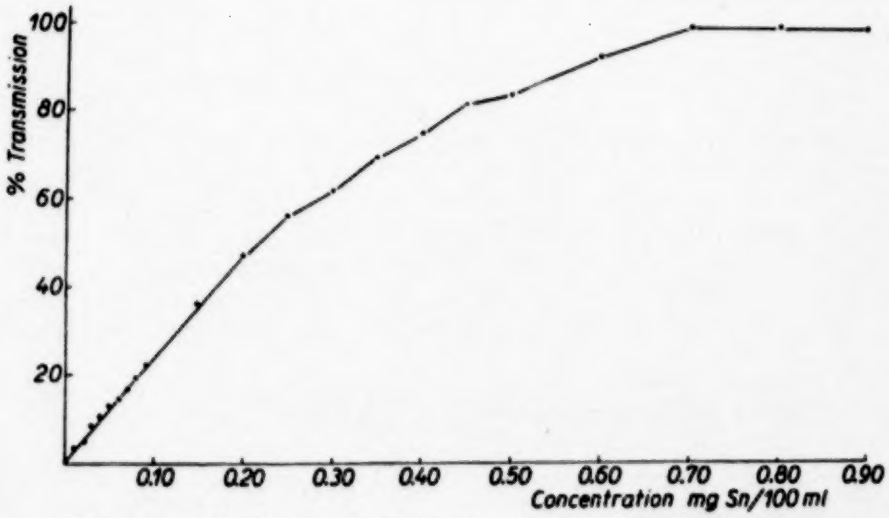

Fig. 3. Effect of concentration of tin on fluorescence.

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described under development of fluorescence, using 10 ml of a standard tin solution containing 1.000 mg Sn/ml. After the addition of the reagent, the fluorescent solution was left to stand for 2 hours and then made up to 1000 ml.

From this solution a series of 22 solutions was prepared by transferring volumes ranging from 1 ml to 90 ml into 100 ml volumetric flasks, adding 10 ml $5N$ NH_4OH and making up to volume. The tin content of these solutions varied from 0.01 mg Sn/100 ml to 0.90 mg Sn/100 ml. It can be seen from Fig. 3 that the fluorescence increases in a fairly linear manner up to a concentration of 0.20 mg Sn/100 ml. From then on up to 0.70 mg Sn/100 ml it increases rather irregularly and above 0.70 mg Sn the fluorescence does not increase any further.

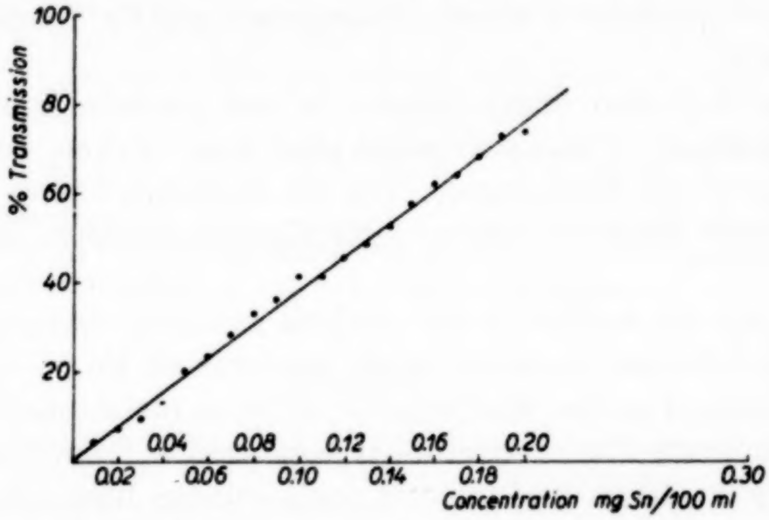

Fig. 4. Linear portion of calibration curve.

The linear section was enlarged by preparing a dilution series of 20 solutions ranging from 0.01 mg Sn/100 ml to 0.20 mg Sn/100 ml. Each solution contained 10 ml $5N$ NH_4OH per 100 ml. From Fig. 4 it is evident that up to 0.20 mg Sn/100 ml there exists linearity between metal concentration and intensity of fluorescence.

Nature of the fluorescent substance

Stannous chloride in acid solution acts on 6-nitro-2-naphthylamine-8-sulphonic acid by reducing the nitro amino compound to the corresponding diamino compound. From a concentrated solution the 2.6-diamino-naphthalene-8-sulphonic acid precipitates as white scales which contain tin in the form of a complex salt. The complex salt is soluble in water with a faint fluorescence and is easily decomposed by the addition of ammonia which precipitates the tin as hydroxide and greatly intensifies the fluorescence of the solution. The tin is also completely removed by recrystallization from $5N$ HCl when the hydrochloride of the 2.6-diaminonaphthalene-8-sulphonic acid crystallizes in form of white needles. This compound is soluble in water with a moderate blue fluorescence which increases strongly on the addition of ammonia. It is the ammonium salt of the 2.6-diaminonaphthalene-8-sulphonic acid which is responsible for the blue fluorescence.

Other compounds, which are known to reduce organic nitrogroups, such as ferrous chloride in acid solution or strong reducing agents such as sodium hyposulphite also give a blue fluorescence with 6-nitro-2-aminonaphthalene-8-sulphonic acid.

Determination of small amounts of tin in copper base alloys

A convenient method for the quantitative determination of small amounts of tin in pure solutions had been developed. Next it was necessary to find out which cations interfered in the determination, by producing fluorescence in solution under similar conditions.

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For this purpose about 12 to 15 mg of the corresponding metal chloride were placed into a 150 ml Erlenmeyer flask, 10 ml 5*N* HCl and 1 g tartaric acid added and heated until dissolved. The solution was then treated as described under development of fluorescence. After standing for 2 hours the solution was observed visually under an ultraviolet lamp for the presence of fluorescence.

Negative results were obtained from As^{+3}, Sb^{+3}, Pb^{+2}, Zn^{+2}, Mn^{+2}, Bi^{+3}, Cu^{+2}, Ni^{+2}, Cr^{+3}, and Ce^{+4}.

UO_2^{+2} and VO^{+2} produce a strong fluorescence and Fe^{+2} and Ti^{+2} cause a very strong fluorescence.

In spite of the fact that many cations do not produce fluorescence under the experimental conditions, it was still found that most of them interfered by causing partial quenching of the fluorescence. The tin therefore has to be separated from other cations present before it can be determined fluorimetrically according to the above method.

In order to apply the method to the analysis of actual materials a procedure was developed to separate and estimate small amounts of tin in copper-based alloys. The separation is based on the precipitation of tin as metastannic acid by dissolving the alloy in nitric acid. The precipitate is separated by centrifuging and dissolved in a mixture of hydrochloric and tartaric acids and the fluorescence developed. The Erlenmeyer flask is replaced with a centrifuge tube of about 60 ml capacity, which has been fitted with a B 19 Quickfit neck. This enables one to perform all operations, *viz.* dissolving, centrifuging and developing of fluorescence in the same vessel.

Procedure

An amount of copper-based alloy containing about 10 mg tin, is weighed into the centrifuge tube and 5 ml concentrated nitric acid added. When the reaction has subsided, the nitric acid is evaporated on a sandbath almost to dryness, but not baked as this decreases the solubility of the metastannic acid. After cooling add 5 ml concentrated nitric acid and 25 ml boiling water and stand in a hot waterbath for one hour.

Place the tube in a centrifuge which has been heated to about 90° C and centrifuge until the precipitate has settled (about 10 minutes). Pour off the clear supernatant solution and wash three times with 5 ml hot 1% NH_4NO_3 solution by centrifuging and decanting. To the metastannic acid precipitate in the tube add 1 g tartaric acid and 10 ml 5*N* HCl. Insert the small funnel fitted with the B 19 cone and pass CO_2 into the tube. Heat the tube gently till the metastannic acid dissolves and the solution clears. Cool, add 1 ml of mercuric chloride solution and 1 ml hypophosphorous acid, heat gently till precipitate coagulates, add 30 ml 5*N* ammonia, cool and add 10 ml of a 1% solution of the reagent. Leave to stand for 2 hours to develop maximum fluorescence and make up to 1000 ml with water. Transfer 10 ml of this solution to a 100 ml volumetric flask, add 10 ml 5*N* ammonia and make up to volume. Measure the fluorescence against the fluorescence of standard tin solutions prepared at the same time as follows:

10 ml of a standard tin solution containing 1.000 mg Sn/ml is treated as described under development of fluorescence and the solution made up to 1000 ml. 100 ml of this solution are further diluted to 250 ml. Aliquots of the fluorescent solution, containing 0.04, 0.08, 0.12, 0.16, 0.20 and 0.30 mg tin are transferred into 100 ml volumetric flasks, 10 ml 5*N* ammonia added and made up to volume. The fluorescence of the solutions is measured, taking the solution containing 0.30 mg Sn as 100% transmission as read on the spectrophotometer scale. From these measurements a calibration curve is plotted which is linear up to a concentration of 0.20 mg Sn/100 ml and is used to determine the concentration of tin in the unknown solution. For most accurate results the ratio of tin to the other constituents present in the unknown solution should be similar to the ratio in the standard tin solutions used for the calibration curve.

Two samples of brass were analysed for tin according to the procedure outlined above. One sample was a NBS 37c standard brass and the other an Analysed Sample for Students. The results are shown in Table III.

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TABLE III

Alloy	*Certified value %*	*Found %*
NBS 37c	0.97	0.94
		0.99
		0.94
Analysed Sample for Students	2.05	2.04
		2.05
		2.02

SUMMARY

A fluorimetric determination for small amounts of tin has been developed using as reagent the ammonium salt of 6-nitro-2-naphthylamine-8-sulphonic acid. The method has been applied to the estimation of small amounts of tin in copper-based alloys.

RÉSUMÉ

Une méthode fluorimétrique est proposée pour le dosage de faibles quantités d'étain, en utilisant comme réactif le sel d'ammonium de l'acide 6-nitro-2-naphtylamine-8-sulfonique. Ce procédé peut être appliqué au dosage de faibles quantités d'étain dans des alliages à base de cuivre.

ZUSAMMENFASSUNG

Eine fluorimetrische Bestimmungsmethode für kleine Zinnmengen wurde vorgeschlagen; als Reagenz dient das Ammoniumsalz der 6-Nitro-2-naphtylamine-8-sulphonsäure. Das Verfahren wurde zur Bestimmung von kleinen Mengen von Zinn in Kupferlegierungen angewendet.

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LA MESURE AUTOMATIQUE DE LA PÉRIODE DE CHUTE DE L'ÉLECTRODE À GOUTTES DE MERCURE, ET SES APPLICATIONS ANALYTIQUES

par

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INTRODUCTION

La concentration d'une substance tensio-active peut être évaluée à partir de la mesure de son activité superficielle (abaissement de la tension superficielle ou interfaciale). Cette méthode permet notamment d'estimer la teneur en constituants tensio-actifs dans les eaux naturelles ou usées, de doser des impuretés dans des produits peu actifs (sucres, acides organiques), d'évaluer le degré de dégradation de certains produits (huiles de transformateur), de caractériser l'efficacité des divers détergents de synthèse (composés cationiques du type ammonium tétrasubstitué, alkylsulfosuccinates alcalins, esters d'alkylarylpolyéthylèneglycol, *etc.* . . .). Ces dosages nécessitent le recours à une courbe d'étalonnage. Les diverses méthodes utilisables (capillaires à dénivellation, techniques d'arrachement, stalagmomètre de Traube) ne fournissent de résultats reproductibles qu'au prix de précautions opératoires assez sévères.

La méthode discutée dans cet article, d'application très générale, consiste à mesurer l'abaissement de la tension interfaciale σ présentée par une surface de mercure, mise en contact avec une solution à laquelle on ajoute la substance tensio-active.

Il résulte des travaux de GOUY[1] et de KUCERA[2] que la tension de polarisation imposée au mercure détermine le taux d'adsorption, en fonction de la charge de la particule et de ses caractéristiques dipolaires. On peut en déduire qu'un choix rationnel de potentiel imposé est susceptible d'améliorer la sélectivité et la sensibilité de la méthode.

La période de chute de l'électrode polarographique peut être considérée, en première approximation, comme proportionnelle à la masse des gouttes formées, cette masse dépendant elle-même de la tension interfaciale cherchée.

Le capillaire polarographique est susceptible de fonctionner de manière extrêmement reproductible et la période de chute peut être déterminée avec une grande précision, grâce à l'emploi d'un timer électronique, comme nous le montrerons dans le présent travail.

Nous nous sommes proposé de reconnaître les possibilités analytiques de la méthode en nous attachant surtout aux points suivants:

a) la mesure même de la période de chute t_g;
b) l'étude de la fonction liant la période de chute t_g à la tension interfaciable σ;
c) l'établissement d'une relation quantitative entre la variation de tension interfaciale σ et la concentration de la substance à doser.

L'étude des relations $\sigma = f(t_g)$ et $\Delta\sigma = f(C)$ n'est pas indispensable car la plupart des dosages s'effectuent à l'aide d'une courbe d'étalonnage. Cette étude est néanmoins très utile car elle permettra de définir les conditions opératoires optima, et de dégager les principales caractéristiques de la méthode, sous le rapport de la précision et de la sensibilité.

Appareillage

Le capillaire utilisé est du type cylindrique. Son rayon intérieur est de l'ordre de $2.8 \cdot 10^{-3}$ cm, la longueur utilisée variant selon les nécessités de l'expérience.

Le réservoir de mercure est disposé à une hauteur supérieure au mètre, de manière à réduire l'importance relative de la contrepression capillaire. La goutte de mercure peut être polarisée par rapport à une électrode de référence à l'aide d'un potentiomètre diviseur à faible résistance.

La mesure de la période de chute s'effectue par voie optique*. La goutte, en tombant, intercepte un faisceau lumineux focalisé à partir d'une source ponctuelle. Chaque passage amène une brusque variation du courant d'une cellule photo-électrique type R.C.A. 1P41 dont la surface sensible est protégée de toute illumination parasite excessive par un écran cylindrique, de manière à assurer un fonctionnement correct sous l'éclairage ambiant normal.

Le signal électrique, amplifié (Fig. 1) par deux étages (6SJ7-6SJ7) à constante de temps élevée, est transformé sous forme d'impulsion (6SN7). Celle-ci est appliquée par couplage diode (6H6) à un étage fonctionnant en échelle de deux bistable (6SN7). La tension de sortie E_v prise en cathode follower ($^1/_2$ 6SN7) passe indéfiniment, et de manière discontinue (en moins de 10 μ sec), aux valeurs 0 et 15 volts à chaque nouvelle chute de la goutte.

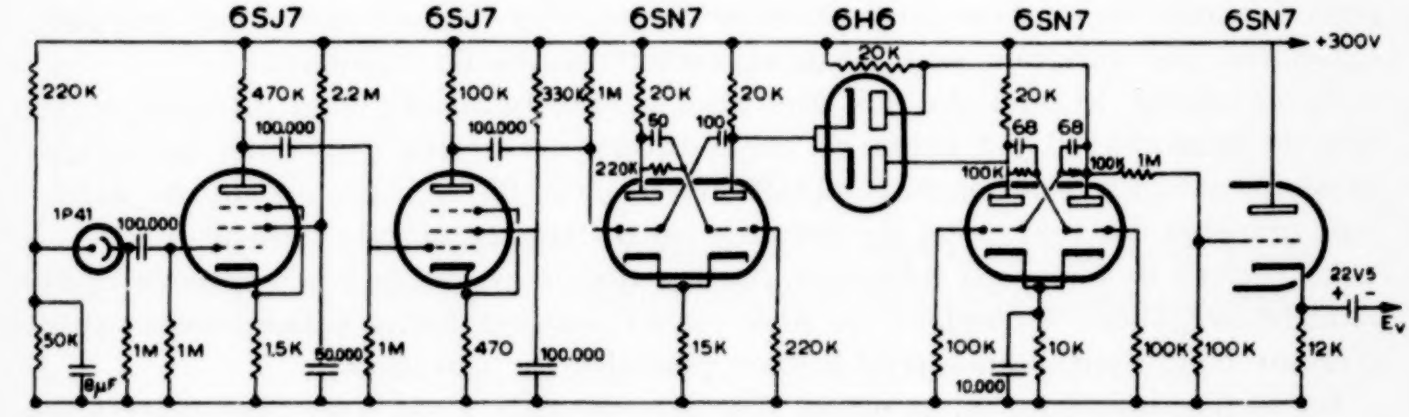

Fig. 1. Switch électronique à commande photoélectrique.

Le chronomètre électronique (Fig. 2) comprend un étage oscillateur piloté par un quartz piézoélectrique de fréquence 10.000 Hz (L.P.E. type ARNM20 thermostatisé). Le signal sinusoïdal est transformé, après amplification, en impulsions carrées ayant les caractéristiques: fréquence 10 kHz, amplitude 30 volts, durée env. 20 μsec. Ces impulsions sont totalisées par une échelle de comptage à 5 étages avec commande de remise à zéro, utilisant les tubes E1T. (La description détaillée des circuits sera trouvée dans Electronic Applic. Bull. no. 1-2, 1953, vol. 14.)

La liaison entre le générateur d'impulsions à 10 kHz et l'échelle de comptage est réalisée par l'intermédiaire d'un tube interrupteur 6L7 qui n'assure la transmission que pour une tension de grille supérieure à + 7 volts. Cette grille est commandée par la tension de sortie E_v du circuit associé à la cellule photoélectrique.

La constante du temps totale du circuit interrupteur est suffisamment faible pour que son fonctionnement soit pratiquement instantané, comparé à la fréquence d'oscillation du quartz.

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* Les mesures basées[5] sur la brusque variation de courant capacitif survenant à chaque chute peuvent être malaisées au voisinage du point de charge nulle, particulièrement en présence d'agents tensio-actifs, dont l'adsorption abaisse notablement la capacité d'électrode.

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L'erreur de mesure est de 0.1 millisec. La dérive en fréquence du quartz reste inférieure à 0.005%.

La détermination de la période de chute s'effectue de la manière suivante: le timer, préalablement mis à zéro, fonctionne dès que la goutte en formation tombe. L'arrêt a lieu au moment de la chute suivante. Le temps est noté, et le timer remis au zéro avant le passage de la troisième goutte, qui déclenche un nouveau chronométrage.

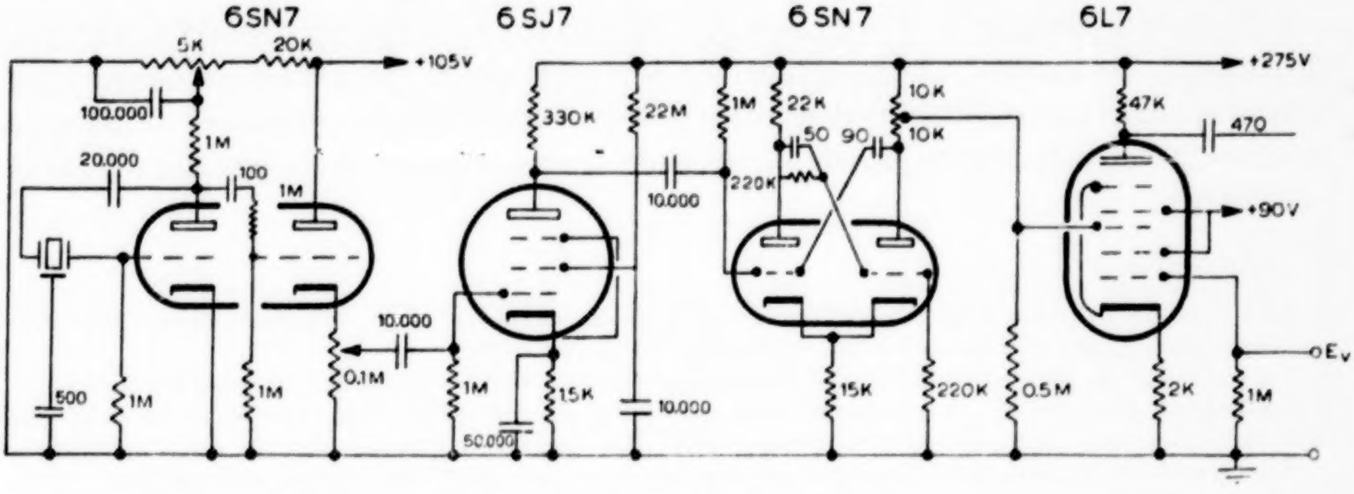

Fig. 2. Générateur d'impulsions à 10 kHz et circuit interrupteur (6L7).

REPRODUCTIBILITÉ SUR LA MESURE DE LA CADENCE DE CHUTE

Le capillaire ne fonctionne de manière reproductible et prolongée que moyennant certaines précautions. Il convient d'éviter les polarisations positives ou négatives excessives, qui amènent la formation de dépôts anodiques ou le dégagement d'hydrogène. L'emploi de solutions concentrées en électrolytes (KCl en particulier) entraîne également une variation sensible de la caractéristique du capillaire.

Après emploi, le capillaire doit être rincé à l'eau bidistillée, sans interrompre le flux de mercure. S'il y a risque de précipitation, il est utile d'effectuer un lavage préalable avec une solution de composition adéquate. Le capillaire est ensuite séché, puis immergé dans un godet de mercure; on interrompt ensuite le débit.

La période de chute est influencée par les vibrations, qui la raccourcissent et la rendent irrégulière. L'emploi d'un socle massif posé sur feutre élimine cette cause d'erreur dont l'importance semble être généralement surestimée.

La section inférieure du capillaire doit être normale à son axe. Tout écart à la verticalité du tube entraîne une diminution notable de la période de chute. L'expérience montre que la période reste pratiquement constante pour des inclinaisons inférieures au degré; elle décroît ensuite à raison d'environ 0.1% par degré. Une telle variation étant aisément décelée avec le chronomètre utilisé, il convient de contrôler la verticalité à moins du degré.

Les mesures de temps ne sont reproductibles que si l'interruption du faisceau lumineux par la goutte est suffisamment brève. Cette condition est réalisée lorsque la distance entre l'extrémité du capillaire et l'axe du faisceau est supérieure au centimètre.

La température modifie simultanément les caractéristiques géométriques du capillaire, la viscosité du mercure et la valeur de la tension interfaciale. Le coefficient de température global, déterminé expérimentalement est cependant peu important: il suffit en pratique, d'assurer la thermostatisation à ± 0.2° C.

En cas d'utilisation prolongée du capillaire, il peut être nécessaire de compenser la décroissance du niveau supérieur du mercure, de manière à maintenir la constance rigoureuse du débit.

La reproductibilité de fonctionnement du capillaire dépend quelque peu de la nature des solutions étudiées, et de leur degré de pureté. D'une manière générale (Tableau I) l'écart type reste inférieur à 0.1%.

TABLEAU I

Milieu	t_g *(sec)*	*Ecart type %*
Eau tridistillée	4.77(38) (34) (32) (37) (38) (39) (42) (30) (30) (36)	0.01
NaOH *M* *	4.38(29) (35) (32) (40) (28) (27) (33) (25) (30) (30)	0.01
NaOH *M* + 1% pyridine	3.33(51) (69) (32) (53) (54) (71) (65) (54) (85) (26)	0.05
Na_2SO_3 0.1 *M*	4.3(191) (191) (145) (180) (162) (183) (187) (208) (205) (207)	0,05

* Préparé à partir d'amalgame de sodium.

RELATION LIANT LA PÉRIODE DE CHUTE t_g À LA TENSION INTERFACIALE σ

La masse maximum M_s d'une goutte de mercure suspendue dans un électrolyte de densité d et formée très lentement, est donnée par la relation de TATE

$$a\, M_s = \frac{2\pi r \sigma}{g} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(I)}$$

(r = rayon intérieur capillaire
g = 981 cm.sec^{-2}
$a = \frac{D-d}{D}$ où D = 13.54)

La masse M_t de la même goutte, détachée du capillaire, est inférieure à cette valeur, du fait que la rupture entre la goutte et la colonne ne s'effectue pas rigoureusement au plan de section du capillaire.

$$M_s = M_t\,(1+\beta) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(II)}$$

Selon HARKINS[3,4]

$$\beta = 3.655\,\frac{r}{M_t^{1/3}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(III)}$$

ou, avec une approximation suffisante,

$$\beta = 19.18\,\frac{r^{2/3}}{\sigma^{1/3}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(IV)}$$

Le terme de correction β vaut environ 0.05 pour le capillaire utilisé (rayon intérieur $2.8 \cdot 10^{-3}$ cm). Sa variation avec σ est relativement peu importante, du fait de l'exposant 1/3: en première approximation, M_t peut être considéré comme proportionnel à σ. En pratique, la présence de substances tensio-actives amène un abaissement $\Delta\sigma$ généralement inférieur à 10%. Dans ces limites, les variations relatives de σ et M_t sont décrites par la relation approchée:

$$\frac{\Delta\sigma}{\sigma} = \frac{\Delta M_s}{M_s} = 0.985\,\frac{\Delta M_t}{M_t} \quad \ldots\ldots\ldots\ldots\ldots \quad \text{(V)}$$

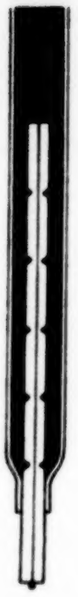

Fig. 3.

Si la cadence de chute est trop rapide, M_t peut prendre des valeurs trop élevées par suite de l'effet cinétique.

L'occurrence éventuelle d'un tel effet a été étudiée en utilisant différentes longueurs d'un même capillaire, à pression de mercure et tension interfaciale constantes. Le capillaire, préalablement entaillé à diverses hauteurs, est entouré d'un tube de Tygon de diamètre supérieur et rétréci à sa base (Fig. 3). Ce dispositif permet de sectionner le capillaire, par un effort exercé sur le tube souple, sans modifier les autres conditions d'expérience.

Les expériences (Tableau II) prouvent que le poids M_t de la goutte varie de moins de 0.1% lorsque t_g varie de 3 à 17 sec. L'effet cinétique est donc absolument négligeable pour des capillaires de très petite ouverture. Les capillaires à cadence rapide (3 à 6 sec) sont, par ailleurs, ceux dont le fonctionnement est le plus reproductible.

TABLEAU II

Na_2SO_3 0.1M $E_{Hg/E.C.S.}$ = 0.60 V, h = 70 cm.

Capillaire	t_g *(sec)*	*Débit (mg/sec)*	M_t *(mg)*
I	17.126	0.43472	7·445
II	11.451	0.6517	7·451
III	6.491	1.1474	7·447
IV	3·547	2.9922	7·446

(II, III, IV, capillaire successivement raccourci).

La relation liant la masse M_t à la période de chute t_g est compliquée par le fait que le débit instantané n'est pas constant[2], la tension interfaciale exerçant une contrepression variable

$$p' = \frac{2\sigma}{R} \quad \text{(où } R \text{ est le rayon instantané de la goutte)} \qquad \text{(VI)}$$

qui s'oppose à la pression de la colonne de liquide.

La contre-pression effective p' correspondant à la durée de vie de la goutte vaut[6]

$$p' = \frac{11.58}{M_t^{1/3}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(VII)}$$

ou encore, avec une approximation suffisante

$$p' = 43.2\ \sigma^{2/3} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(VIII)}$$

Cette contre-pression correspond à une colonne de mercure de hauteur $h' = 0.0326\ \sigma^{2/3}$ et le débit moyen varie avec σ selon $\boldsymbol{m} = k(h - 0.0326\ \sigma^{2/3})$ . . . . (IX)

$$\text{Par ailleurs, } M_t = \boldsymbol{m}\,.\,t_g \quad \ldots\ldots\ldots\ldots\ldots \quad \text{(X)}$$

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Dans les conditions expérimentales proposées et pour des abaissements de tension interfaciale inférieures à 10%, les variations relatives de M_t et t_g sont données par

$$\frac{\Delta M_t}{M_t} = 0.988\,\frac{\Delta t_g}{t_g} \quad \ldots\ldots\ldots\ldots\ldots \quad \text{(XI)}$$

Finalement, la tension interfaciale est liée à la période de chute t_g par la relation

$$\sigma = \frac{\alpha\, g\, k}{2\,\pi\, r}\left(1 + 19.18\,\frac{r^{2/3}}{\sigma^{1/3}}\right)(h - 0.0326\,\sigma^{2/3})\,t_g \quad \ldots \quad \text{(XII)}$$

Par ailleurs, dans les limites définies par les conditions expérimentales proposées,

$$\frac{\Delta\sigma}{\sigma} = 0.97_3\,\frac{\Delta t_g}{t_g} \quad \ldots\ldots\ldots\ldots\ldots \quad \text{(XIII)}$$

Le facteur de proportionnalité peut être rapproché de l'unité, en utilisant un capillaire de rayon inférieur, et une colonne de mercure de hauteur plus grande.

RELATION ENTRE LA CONCENTRATION DE LA SUBSTANCE TENSIO-ACTIVE ET LA DIMINUTION Δt_g DE LA PÉRIODE DE CHUTE

Dès que la concentration C de la substance à doser est suffisante pour que le film adsorbé soit pratiquement compact, on a, à tension d'électrode maintenue constante, et avec le capillaire décrit

$$\Gamma m = \frac{\partial\sigma}{R\,T\,\partial\ln C} \simeq \frac{0.973\cdot\sigma\cdot\partial t_g}{R\,T\,t_g\ln C} = k'\,\frac{\partial t_g}{R\,T\,\partial\ln C} \quad \text{(XIV)}$$

L'excès superficiel Γm vaut environ $4\cdot10^{-10}$mol g.cm^{-2}, la majorité des particules adsorbables ayant une surface moléculaire d'adsorption comprise entre 30 et 50 Å^2.

k' Se détermine expérimentalement à partir d'une solution de pouvoir tensio-actif connu.

La relation (XIV) permet de calculer que l'imprécision sur C est de l'ordre de 5%, celle affectant $\frac{\Delta t_g}{t_g}$ étant d'environ 0.15%.

Cette imprécision est indépendante de la concentration pour autant que la quantité adsorbée varie peu avec C, ce qui est généralement le cas (toutefois, si la concentration ou l'adsorbabilité de la substance dosée est faible, l'excès superficiel peut être sensiblement inférieur à Γm, ce qui peut entraîner un amoindrissement significatif de la précision).

Des expériences systématiques, effectuées avec diverses substances tensio-actives, confirment cette conclusion: dans un large domaine de concentration, la fonction $\Delta t_g = \mathrm{f}(\ln C)$ est pratiquement linéaire, la pente variant assez peu avec la nature de la substance (Fig. 4). L'imprécision relative sur C est donc à peu près identique dans tous les cas.

La sensibilité par contre est très variable: elle est fonction directe de l'adsorbabilité, que l'on peut évaluer par l'intersection des droites extrapolées jusqu'à l'axe des abscisses.

La tension superficielle, calculée à partir de la cadence de chute, cesse d'avoir une signification réelle lorsque le film adsorbé n'est pas en équilibre avec la solution.

Or, l'édification du film peut entraîner un appauvrissement partiel des particules adsorbables, la composition locale étant alors différente de la composition volumique. Un tel effet ne tend à devenir important que lorsque la concentration en soluté est très faible. Ce cas peut se présenter lors de l'analyse de substances à pouvoir tensio-actif extrêmement élevé, et il est utile d'évaluer la limite de sensibilité de la méthode résultant de cette cause d'erreur.

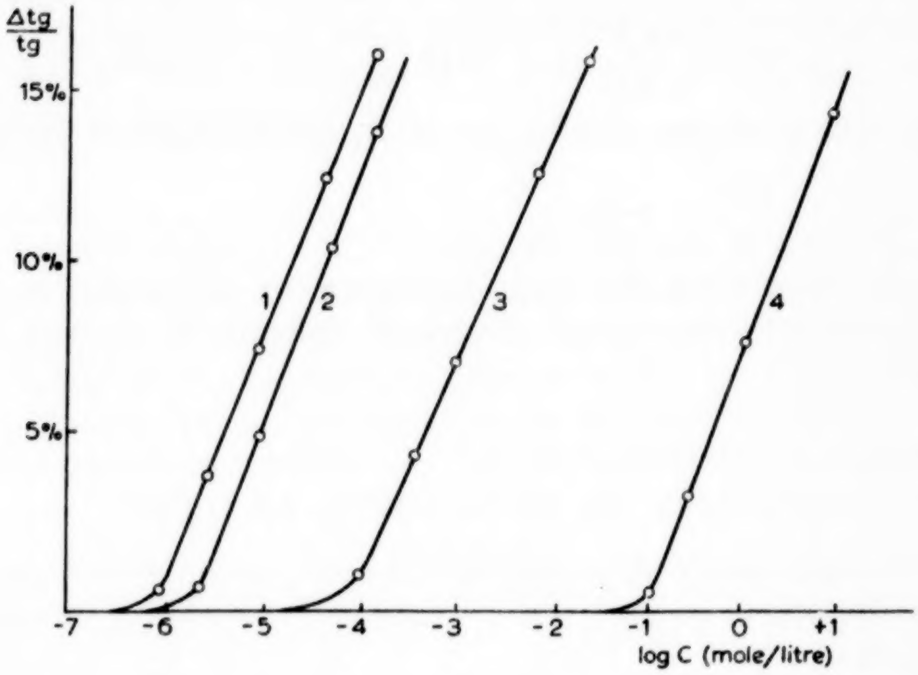

Fig. 4. Influence de la concentration de diverses substances tensio-actives sur la variation de la période de chute.
1. Milieu K_2SO_4 0.1 M + Synkapon UCB (alkylsulfosuccinate alcalin).
2. Milieu K_2SO_4 0.1 M + Aminol UCB „pur" (alkyldiméthylbenzylamine).
3. Milieu K_2SO_4 0.1 M + benzylamine.
4. Milieu NaOH M + pyridine.

Considérons le cas simple où le film est compact. Dans les conditions expérimentales définies précédemment (débit $m \cong 2$ mg.sec^{-1}, $t_g \cong 3.5$ sec), le nombre de particules adsorbées vaut, si la surface occupée par la molécule est de 50 Å^2

$$N_{\text{ads}} \cong \frac{0.85 . m^{2/3} \, t_g^{2/3}}{50 . 10^{-16}} \cong 7.3 \cdot 10^{12} \quad \ldots\ldots\ldots\ldots \quad \text{(XV)}$$

Durant la période de vie de la goutte, le nombre maximum de particules susceptibles de diffuser vers l'électrode vaut

$$N_{\max} = \frac{N_\circ}{F} \, 706 \sqrt{D} . C . m^{2/3} t_g^{7/6} \cong 7 . 10^{21} . C \quad \ldots\ldots \quad \text{(XVI)}$$

(D = coefficient diffusion cm^2.sec^{-1}
$N_\circ$ = nombre d'Avogadro)

On peut considérer que l'effet d'appauvrissement local est négligeable lorsque $10^{-2} N_{\max} > N_{\text{ads}}$.

Cette condition est remplie lorsque $C > 10^{-7} M$.

Pour des concentrations inférieures à cette limite, les valeurs calculées dépendent de manière complexe des caractéristiques du capillaire, et cessent d'avoir une signification quelconque.

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APPLICATIONS ANALYTIQUES

L'étude des facteurs influençant la variation de la période de chute a permis de tirer les conclusions suivantes:

1) t_g est pratiquement proportionnel à σ, si l'on utilise un capillaire polarographique normal et une hauteur de mercure de l'ordre du mètre;
2) à l'aide de l'appareil décrit, et moyennant l'observance de quelques précautions, t_g peut être évalué à moins de 0.15%. La précision correspondante sur C, peu dépendante de la valeur de C, est de l'ordre de 5% dans les cas favorables;
3) la méthode cesse d'être utilisable aux concentrations inférieures à $10^{-7} M/l$.

En pratique, les dosages s'effectuent à l'aide d'une courbe d'étalonnage préalablement construite. La solution est rendue conductrice par addition d'un électrolyte-support. Un choix judicieux du sel employé peut permettre d'exalter l'activité superficielle de la substance à doser. La tension de polarisation sera ajustée en fonction de la charge éventuelle de la particule.

Les caractéristiques générales de la méthode sont les suivantes:
précision moyenne, de l'ordre de quelques pourcents;
mesures rapides et reproductibles;
sensibilité variant selon l'activité de la substance à doser;
sélectivité faible, susceptible d'être accrue par le choix du support et de la tension de polarisation.

RÉSUMÉ

On décrit un chronomètre électronique commandé par cellule photoélectrique, permettant de mesurer la cadence de chute de l'électrode à gouttes de mercure, avec une précision supérieure à 0.1%.

On analyse la relation liant la période de chute à la concentration des substances tensio-actives présentes en solution.

Les applications analytiques sont brièvement discutées.

SUMMARY

A description is given of an electronic chronometer, controlled by a photo-electric cell, which enables one to measure the drop rate of the dropping mercury electrode to an accuracy of within 0.1%.

The relation between the drop rate and the concentration of surface-active agents is discussed and the analytical potentialities of the method are briefly examined.

ZUSAMMENFASSUNG

Ein mit einer Photozelle verbundener elektronischer Chronometer wird beschrieben, welcher die Quecksilbertropfzeit mit einer Genauigkeit von mindestens 0.1% zu messen erlaubt.

Die Beziehung zwischen der Fallzeit und dem Gehalt an oberflächenaktiven Stoffen wird untersucht.

Analytische Anwendungen werden kurz erörtert.

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UN TRANSITOMÈTRE DE PRÉCISION

par

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I. INTRODUCTION

L'électrolyse sous courant constant en solution non agitée constitue une méthode analytique d'utilisation récente[1 à 5], dont les principales caractéristiques ont été discutées dans ce journal[5]; quoique moins sensible que la méthode polarographique, elle présente sur celle-ci divers avantages liés à sa rapidité, sa précision, et au moindre coût de l'appareillage, celui-ci étant par ailleurs susceptible d'un fonctionnement entièrement automatique.

Les facteurs sensibilité, précision et rapidité de manipulation dépendent essentiellement du type d'électrode utilisée. Les électrodes solides, irremplaçables lorsqu'il s'agit de doser des substances très oxydantes, possèdent une surface de caractéristiques physicochimiques mal définies et de capacité électrique élevée. Elles sont aisément polluées par des substances adsorbables ou des produits d'électrodéposition. La nappe de mercure constitue une électrode renouvelable, où ces facteurs défavorables sont pratiquement éliminés, mais dont la surface géométrique dépend d'effets de ménisque et de mouillage latéral, qu'il est difficile de contrôler initialement, et qui varient au cours des polarisations successives; le renouvellement du mercure est, par ailleurs, une opération dont la reproductibilité reste inférieure au pourcent[3].

L'emploi d'une électrode à goutte de surface contrôlée résout ces difficultés. En pratique, on a intérêt à utiliser une électrode dont la période de chute dans l'eau est de l'ordre de la minute, et qui est polarisée sous courant constant quelques dizaines de secondes avant sa chute.

La surface géométrique peut être aisément reproduite à moins du millième, à l'aide d'un dispositif retardateur dont la mise en marche est synchronisée avec la chute de la goutte préexistante.

De manière à rendre négligeables les effets d'expansion et de sphéricité de la surface, la durée de transition associée à la décharge de la particule à doser ne peut pas excéder quelques décisecondes. Cette condition, liée au principe de fonctionnement de l'électrode, impose à son tour les caractéristiques de l'appareillage de mesure qui doit être adapté à l'analyse d'un phénomène transitoire relativement rapide. L'insuffisance en précision de l'oscilloscope à rayons cathodiques nous a amené à lui substituer un appareil automatique, le transitomètre[5], qui mesure la

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durée nécessaire t_{E_x} pour que le potentiel de l'électrode atteigne toute valeur arbitraire E_x. En dehors de ses applications analytiques, l'appareil trouve d'autres utilisations dans l'étude de la cinétique des réactions d'électrode. Le temps t_{E_x} mesuré à un potentiel judicieusement choisi est lié à la concentration cherchée par la relation de SAND[1 à 6], si la concentration est supérieure à $10^{-3}N$, et la réaction d'électrode non exagérément irréversible. Dans les autres cas, le dosage peut s'effectuer à l'aide d'une courbe de calibrage $t_{E_x} = f(C)$.

L'objet de cette communication est d'exposer le principe de fonctionnement, de décrire les circuits et d'analyser les caractéristiques de service d'un transitomètre de précision, susceptible d'effectuer des dosages avec une imprécision inférieure à 0.2% dans les cas favorables. Cette exigence nécessite le contrôle du courant d'électrolyse à moins de 0.1%, la mesure du temps de transition à ± 0.1 millisec et une reproductibilité sur E_x de l'ordre de ± 0.5 mV, la surface de l'électrode étant connue à mieux de 0.05%. L'appareillage doit également, autant que possible, fonctionner de manière automatique, permettre une sélection rapide de l'intensité imposée et du potentiel E_x et assurer la protection de l'électrode en interrompant le courant de polarisation dès que la mesure chronométrique est terminée.

II. PRINCIPE DE FONCTIONNEMENT (Fig. 1 et 2)

Le courant d'excitation de la chaîne de relais RIA (ou RIB) prend les valeurs 0 ou 6 mA, de manière discontinue et réversible, selon que la tension d'entrée, mesurée en A (ou en B) par rapport à la masse, est très légèrement négative ou positive (à moins de 1 mV).

Le circuit trigger utilisé est celui décrit par MÜLLER ET LINGANE[7].

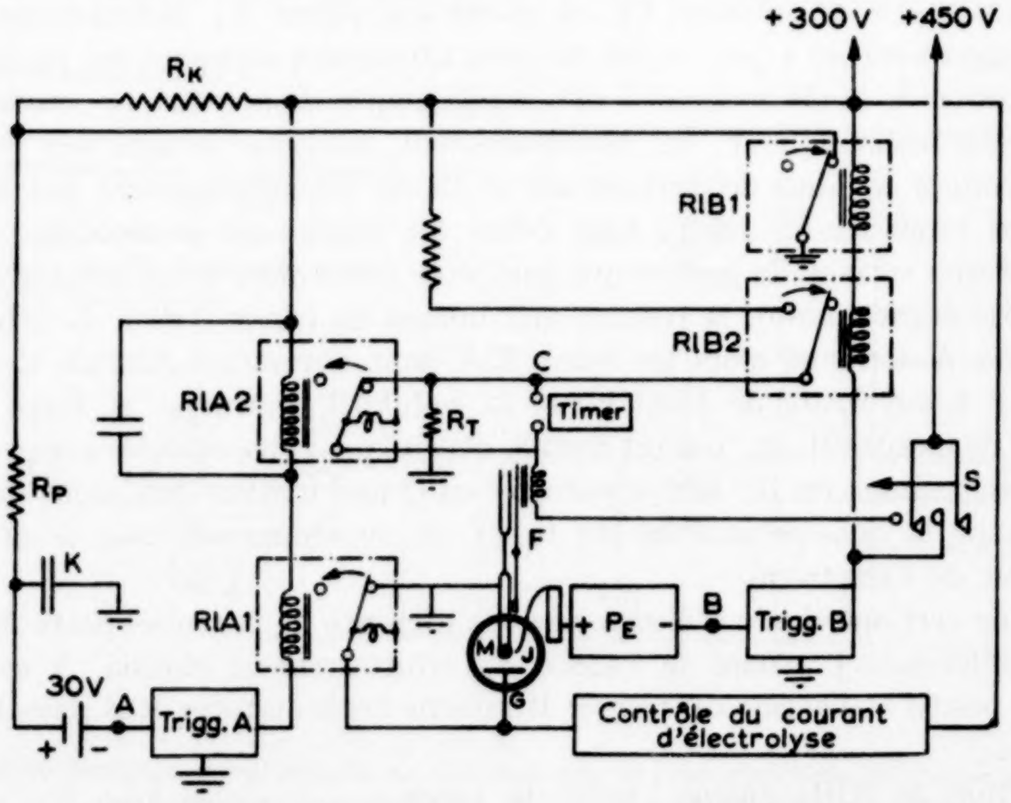

Fig. 1. *Schéma de principe*

RIA1, RIA2: relais monostables
RIB1, RIB2: relais bistables polarisés
M : électrode de mesure
J : électrode de référence
G : électrode auxiliaire.

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Le courant d'excitation tend à déplacer l'armature des relais dans le sens des flèches. Les relais RIA sont monostables et, en l'absence de courant, prennent la position figurée. Les relais RIB sont du type bistable polarisé. Le rappel de leur armature dans le sens opposé aux flèches s'obtient en lançant, par la clé S, un courant de sens inversé.

Soit à déterminer le temps nécessaire pour que le potentiel de l'électrode de mesure M atteigne, pour un courant d'électrolyse donné, la valeur arbitraire E_x, par rapport à l'électrode de référence J.

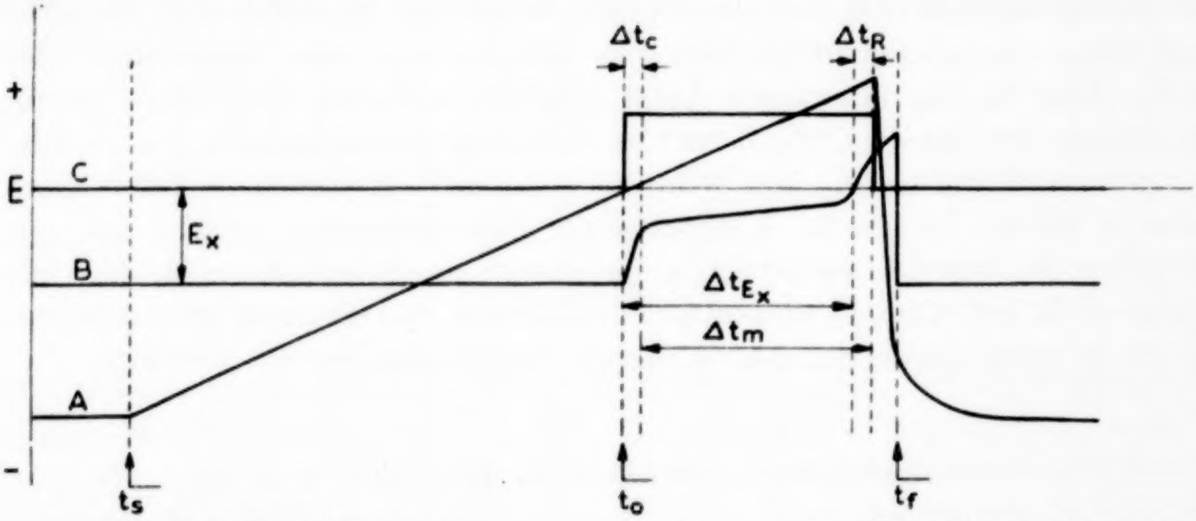

Fig. 2. *Chronologie de fonctionnement*

t_s : enclenchement de la clé S
t_0 : début de l'électrolyse
t_f : retour à l'état initial
courbes A.B.C.: potentiels mesurés aux points correspondants de la Fig. 1.
E_x : potentiel arbitraire fixé par P_E (Fig. 1)
$\triangle t_{Ex}$: durée effective à mesurer
$\triangle t_R$: retard d'arrêt du timer
$\triangle t_c$: retard de compensation
$\triangle t_m$: durée mesurée

Le potentiomètre de précision P_E est ajusté à la valeur E_x. Initialement, les deux circuits trigger sont au repos, et les diverses armatures occupent les positions de la Fig. 1. L'action de la clé à rappel S détache la goutte de mercure préexistante par le rupteur électromécanique F, et, simultanément, renverse le sens des relais RIB. Le condensateur K, ainsi décourtcircuité se charge progressivement par R_K et R_P.

Après un intervalle de temps bien défini (de l'ordre de 30 secondes, et auquel correspond une surface de goutte qui peut être déterminée avec précision, le débit du capillaire étant connu), la tension aux bornes du condensateur K atteint 30 V.

Le trigger A actionne alors les relais RIA dont l'armature bascule dans le sens des flèches. L'ouverture de RIA1 libère la cellule d'électrolyse et force à travers l'électrode de mesure M, un courant dont la densité peut être calculée avec exactitude. Le décourtcircuitage de R_T fait apparaître en C une tension de l'ordre de + 15 V, qui enclenche la mise en marche du timer, en synchronisme avec le début de la polarisation de l'électrode.

Après une certaine durée d'électrolyse, la différence de potentiel entre M et l'électrode de référence J atteint la valeur E_x arbitrairement choisie. A cet instant, B devient positif et l'action du trigger B ramène les armatures RIB dans la position du schéma.

L'ouverture de RIB2 amène l'arrêt du timer.

La fermeture du circuit RIB1 provoque l'extinction du trigger A (R_P agissant en pare-étincelle) et le retour des armatures RIA à la position figurée.

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Le courtcircuitage de la cellule d'électrolyse entraîne finalement l'extinction du trigger B, ce qui reste sans action sur les relais RlB, ceux-ci étant bistables.

La succession automatique de ces diverses opérations ramène l'ensemble des circuits à leur état initial, et une nouvelle action de la clé S entraîne la répétition identique du fonctionnement décrit, le début de la polarisation s'effectuant sur une électrode renouvelée, et de caractéristique géométrique constante.

Du fait de l'inertie d'action des relais utilisés (très faible mais non absolument négligeable) le temps mesuré par le timer est légèrement supérieur au temps réel (Fig. 2, courbe C). L'inertie du relais RlB2 introduit une erreur par excès de l'ordre de 0.9 millisec. Cette erreur est éliminée en retardant d'une durée équivalente l'ouverture de RlA2 par rapport à RlA1, à l'aide d'une capacité de valeur judicieusement choisie connectée aux bornes de RlA2.

Toutes les opérations commandées par les relais, dont l'irreproductibilité pourrait influencer la précision de la mesure, s'effectuent par *ouverture* du circuit de l'armature. Cette disposition élimine divers inconvénients (étincelle, rebond, délai de transit) et, jointe à l'utilisation de courants d'excitation largement calculés, réalise des conditions de fonctionnement en exigence avec les caractéristiques du timer[9]. Celui-ci permet la mesure de toute durée inférieure à 100 sec à ± 0.1 millisec, l'imprécision relative étant inférieure à 0.005%.

III. DESCRIPTION

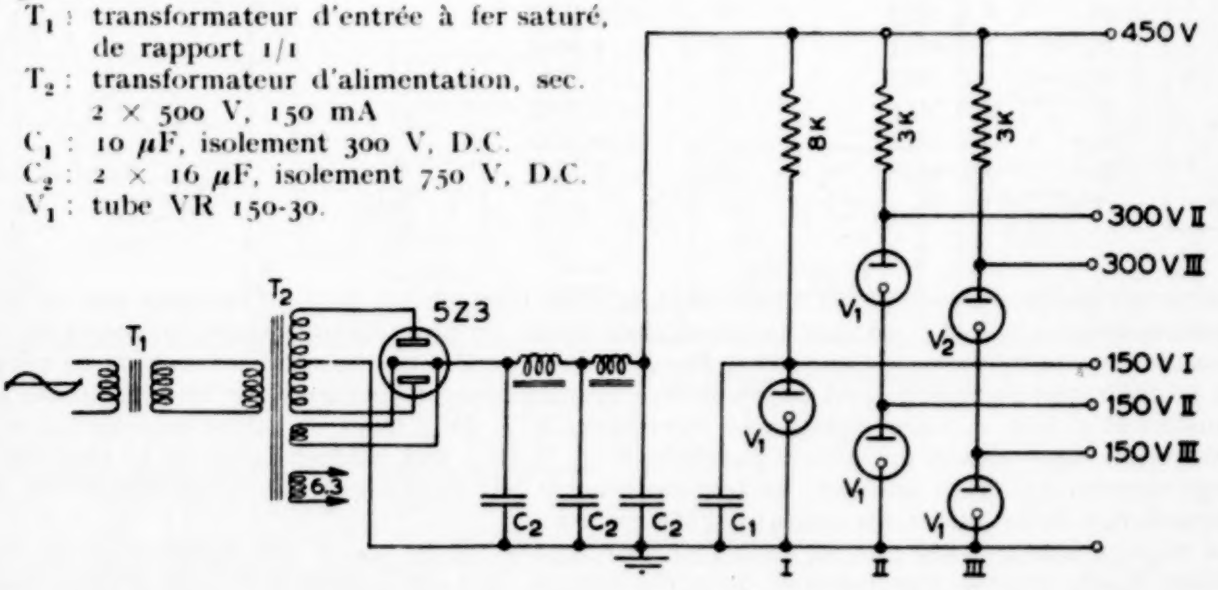
Alimentation générale (Fig. 3)

Du type conventionnel, elle fournit les tensions continues + 450 V, + 300 V et + 150 V.

La stabilisation est assurée par un transformateur d'entrée à fer saturé, et des tubes-néon de type VR 150-30. Les trois chaînes I, II, et III alimentent ces circuits à exigence de stabilité décroissante, les tensions C étant utilisées par les éléments à consommation discontinue.

Fig. 3. *Bloc d'alimentation*

T_1 : transformateur d'entrée à fer saturé, de rapport 1/1
T_2 : transformateur d'alimentation, sec. 2 × 500 V, 150 mA
C_1 : 10 μF, isolement 300 V, D.C.
C_2 : 2 × 16 μF, isolement 750 V, D.C.
V_1 : tube VR 150-30.



Circuit d'électrolyse (Fig. 4)

La constance du courant est assurée en utilisant une tension stabilisée de l'ordre de quelques centaines de volt, débitant dans une résistance de charge stable. La force contre-électromotrice $\triangle E$ développée par la cellule d'électrolyse n'exerce qu'une action négligeable, qui peut être réduite à moins de 0.1%, en ajustant le potentiomètre de contrepolarisation P_4 à la valeur moyenne de $\triangle E$.

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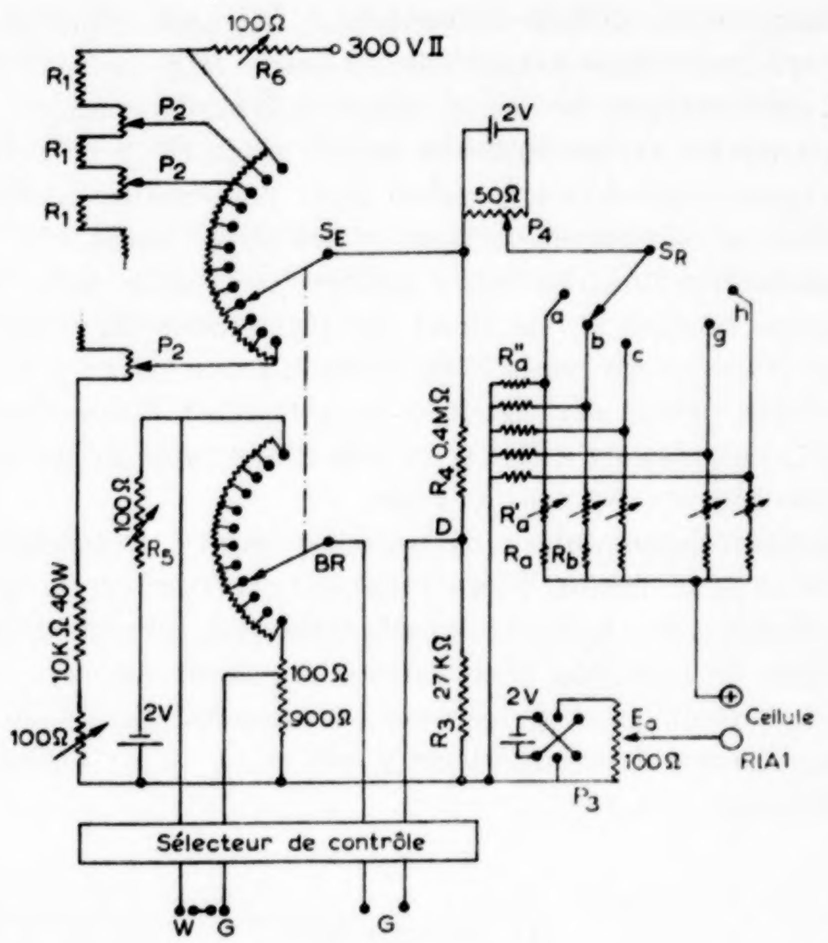

Fig. 4. *Circuit d'électrolyse*

R_1 : 1000 ohms 10 W ajustable
P_2 : 250 ohms 5 W
BR : élément de décade Cambridge 10 × 100 ohms
W : élément Weston type Cambridge L 269286
G : galvanomètre de zéro type Cambridge 41159/3
R_a : 25.6 MΩ R''_a : 202 KΩ
R_b : 12.8 MΩ R''_b : 203 KΩ
R_c : 6.4 MΩ R''_c : 206 KΩ
R_d : 3.2 MΩ R''_d : 213 KΩ
R_e : 1.6 MΩ R''_e : 228 KΩ
R_f : 0.8 MΩ R''_f : 266 KΩ
R_g : 0.4 MΩ R''_g : 400 KΩ
R_h : 0.2 MΩ R''_h : 8 MΩ
$R'_{a,b}$: 0.05 $R_{a,b...}$

Le circuit décrit permet, par la commande de deux sélecteurs à plots, d'imposer des intensités comprises entre 2 mA et 8 μA, par valeurs échelonnées, en progression relative de moins de 10%.

Les diverses résistances de charge R_a, R_b . . . sélectionnées par S_R, ont des valeurs en progression géométrique de raison 2, et peuvent être éventuellement corrigées par les résistances additionnelles R'_a, R'_b . . . Les résistances auxiliaires R''_a, R''_b sont calculées de telle façon que la résistance équivalente du circuit parallèle $R + R'/R''$ soit indépendante de la résistance de charge choisie. De cette manière, la tension fournie par le diviseur potentiométrique S_E reste indépendante de la valeur du courant d'électrolyse.

La tension sélectionnée par S_E peut être prise entre 150 et 300 V par échelons de 15 V. Le diviseur R_4-R_3 prélève une fraction de cette tension, qui est comparée à celle fournie par un potentiomètre de précision dont l'élément sélecteur BR est couplé axialement à S_R. Ce potentiomètre est alimenté par batterie, et calibré par R_5 à l'aide d'un élément Weston.

Les variations éventuelles des résistances R_1 sont périodiquement compensées par les potentiomètres P_2, les légères fluctuations de tension qui pourraient survenir en cours de fonctionnement étant corrigées par R_6.

Le potentiomètre auxiliaire P_3 permet de prépolariser l'électrode de mesure par rapport à l'électrode auxiliaire, à toute tension $E_\circ$ comprise entre + et — 2 V.

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Circuits de mesure et d'automatisation (Fig. 5)

Leur description, limitée à quelques particularités d'ordre technique, complète l'exposé du principe de fonctionnement et le diagramme de la Fig. 5.

Les circuits ,,trigger'' utilisent une double triode 6SN7 opérant en montage de SCHMITT[7,8], avec une résistance de cathode commune de 200 ohms. Ce tube est lié par couplage direct à une pentode préamplificatrice du type 6SJ7.

La polarisation de cathode du tube 6SJ7 du trigger B doit être fixée avec précision à une valeur telle que le basculement survienne à potentiel de grille zéro.

Le contrôle et l'ajustage de cette polarisation sont assurés par les circuits de la clé B_2 et le tube indicateur au néon V 4.

Lorsque la clé est en sa position stable (1), la grille est polarisée négativement par rapport à la masse par P_E et l'élément du tube 6SN7, qui commande le fonctionnement des relais, est non-conducteur.

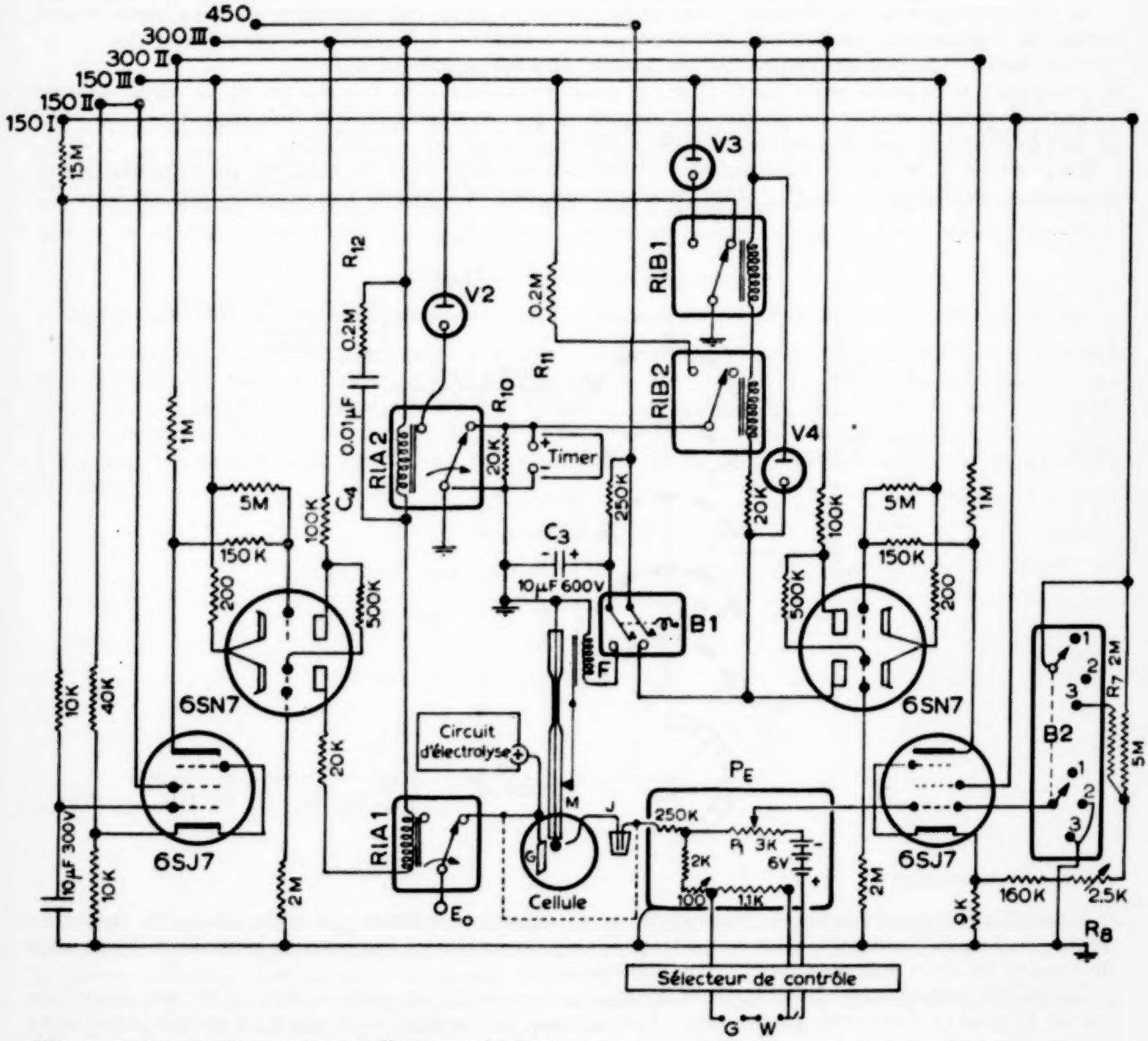
450
300 III
300 II
150 III
150 II
150 I
15M
V3
RIB1
RIB2
R12
0.2M
V2
0.2M
R11
0.01μF
R10
RIA2
20K
Timer
+
-
C4
V4
1M
5M
150K
200
100K
500K
250K
20K
100K
5M
150K
200
1M
500K
C3
10μF 600V
B1
F
6SN7
6SN7
10K
40K
20K
Circuit d'électrolyse
PE
B2
R7 2M
5M
1
2
3
6SJ7
6SJ7
10μF 300V
10K
2M
RIA1
E0
M
J
G
Cellule
250K
P1 3K
2K
6V
100
1.1K
2M
9K
160K
2.5K
R8
Sélecteur de contrôle
G
W

Fig. 5. *Circuits de mesure et d'automatisation*

B_1: clé à rappel (2 plots)
B_2: clé à rappel (3 × 2 plots — position stable 1)
G : électrode auxiliaire
J : électrode de référence
M : électrode de mesure
V_2, V_3, V_4: voyants de contrôle, type 110 V néon
RIA1,2: relais télégraphiques monostables, type Siemens T rls 67 a, Tbv 3704/14
RIB1,2: relais télégraphiques bistables polarisés, type Siemens T rls 64 a, Tbv 3402/14
P_1: potentiomètre de précision, type Colvern CLR 8205.

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En position intermédiaire (2), la grille est mise à la masse; dans ces conditions, le trigger doit s'actionner, ce qui est signalé par l'allumage de V 4.

En position extrême (3), la faible variation de la tension de cathode (de l'ordre de + 0.7 millivolt), obtenue par la mise en circuit de R_7, doit suffire à ramener le trigger au repos, décelé par l'extinction de V 4. L'ajustage de la tension de cathode s'effectue par la résistance variable R_8. Si la tension est convenablement réglée, V 4 ne s'allume qu'en position 2. L'allumage en position 2 et 3, et l'extinction sur toutes les positions correspondent respectivement à une tension de cathode trop forte ou trop faible.

Le néon de contrôle V 2 s'allume pendant toute la durée de fonctionnement de l'appareil, depuis l'enclenchement de la clé B_1 jusqu'au retour aux conditions initiales (de t_s à t_f — Fig. 2) V 3 signale l'intervalle de temps où l'électrode est polarisée (de t_0 à t_f — Fig. 2).

Circuit de contrôle (Fig. 6)

Ce circuit comprend un élément Weston de précision et un galvanomètre de zéro, dont divers modes de connection, assurés par un sélecteur de 5 galettes à 5 positions, permettent de:

1) standardiser le potentiomètre PE en valeur absolue (position 4);
2) comparer la tension prise en D (Fig. 4) proportionnelle à la tension en SE, à celle fournie par un potentiomètre de précision commandé par le sélecteur BR (position 3);
3) standardiser ce potentiomètre en valeur absolue (position 2, par R_5).

En position 3, la valeur du courant d'électrolyse est contrôlée de manière permanente, toute fluctuation supérieure à 0.05% étant aisément décelée et corrigée par la résistance variable R_6.

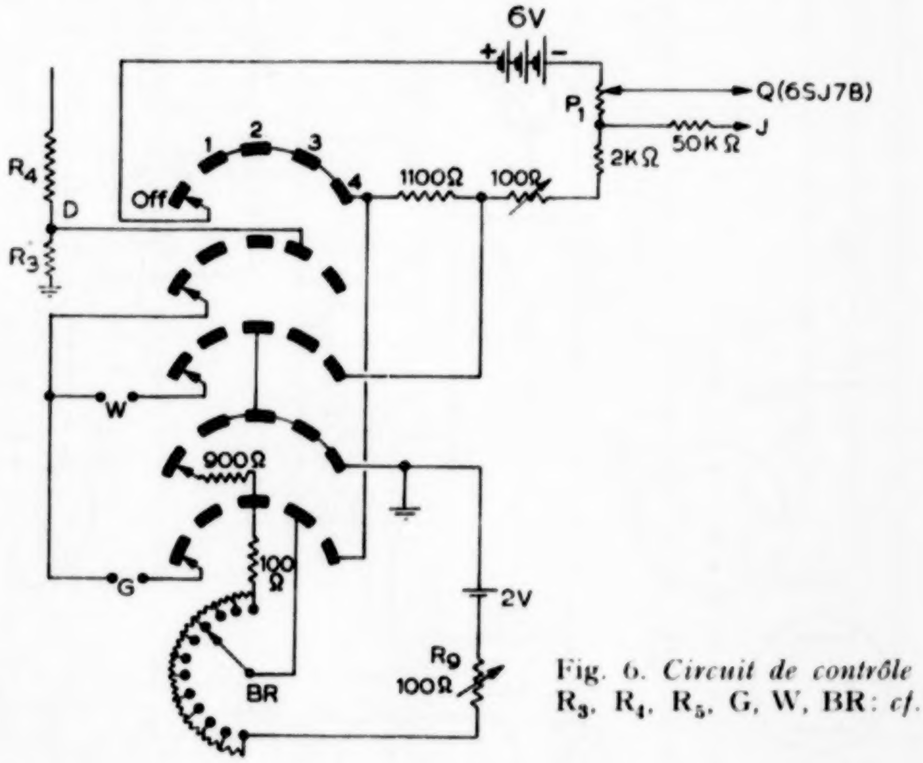

Fig. 6. *Circuit de contrôle*
R_3, R_4, R_5, G, W, BR: *cf.* Fig. 4.

Électrode de mesure

L'électrode à goutte de mercure consiste en un capillaire cylindrique, d'un diamètre intérieur de l'ordre de $4 \cdot 10^{-3}$ mm étiré dans sa partie médiane, de manière à réaliser une période de chute libre de l'ordre de deux minutes dans l'eau distillée.

Le circuit retardateur du trigger A enclenche le courant de polarisation pour une durée de vie de la goutte d'environ 30 secondes. Les valeurs de l'intensité du courant d'électrolyse sont choisies de telle manière que la durée utile de la polarisation soit de l'ordre de la déciseconde.

Dans ces conditions, les effets d'expansion de surface et de sphéricité du champ de diffusion sont entièrement négligeables.

La chute de la goutte préexistante est obtenue par décharge de la capacité C_3 dans l'électroaimant du marteau frappeur.

Le capillaire décrit est susceptible d'un fonctionnement prolongé et très reproductible, au prix des précautions suivantes:

1) après utilisation: rinçage méticuleux, séchage, puis immersion dans un godet de mercure, ces opérations étant effectuées sans interrompre le débit;
2) choc ajusté de manière à assurer la chute de la goutte, sans amener de vibrations excessives entraînant la rupture de la colonne de mercure.

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Il convient également d'éviter de prolonger la polarisation de l'électrode à des tensions excessives; ce risque est entièrement éliminé avec l'appareillage décrit, qui interrompt la polarisation de l'électrode dès que le potentiel préfixé est dépassé.

L'électrode auxiliaire peut être constituée par une nappe de mercure. Dans de nombreux cas, son potentiel est suffisamment stable pour pouvoir être pris comme référence, ce qui évite l'emploi d'une électrode supplémentaire.

Chronomètre électronique

Le timer utilisé, déjà décrit dans ce périodique[9], comprend un générateur d'impulsions à 10 Kc, qui actionne une échelle de comptage à 5 décimales munie de tubes Dekatron E1T, par l'intermédiaire d'un tube bigrille 6L7 agissant comme interrupteur dès que la tension d'entrée est abaissée en dessous de + 7 V par rapport à la masse. Cette tension est fixée par le diviseur potentiométrique R_{10} et R_{11} et les relais RlA2 et RlB2 qui en assurent la discontinuité.

IV. CARACTÉRISTIQUES DE FONCTIONNEMENT

Les circuits décrits fournissent un courant de polarisation dont la valeur est connue à mieux de 0.1%, le potentiel E_x étant déterminé à environ ± 0.4 mV. Par ailleurs, l'imprécision du chronomètre électronique est de ± 0.1 millisec.

Les expériences détaillées ci-dessous, où la cellule d'électrolyse est remplacée par divers éléments de circuit, permettent de définir les caractéristiques de l'appareil en régime de fonctionnement.

1. *Reproductibilité de fonctionnement des relais. Ajustage du retard de compensation* $\triangle tc$ (Fig. 2)

La cellule de mesure est remplacée par une résistance ohmique de valeur telle que le courant de polarisation choisi y développe une tension de l'ordre du volt. La borne positive de la résistance est connectée au potentiomètre P_E, ajusté à une valeur E_x inférieure au volt. Dans de telles conditions, la tension E_x est dépassée dès l'instant initial de la polarisation, et le temps à mesurer est nul. En pratique, il en est autrement, du fait du retard d'action du relais RlB2 (Tableau I).

TABLEAU I

Temps réel: 0.0 millisec. Circuit C_4, R_{12} déconnecté.

Temps mesuré	*Fréquence de la mesure*
0.6	0
0.7	4%
0.8	18%
0.9	48%
1.0	28%
1.1	2%
1.2	0

Le retard moyen est de 0.91 millisec. L'ordre de grandeur de l'écart-type (0.05 millisec) permet de conclure que l'irreproductibilité de fonctionnement des relais n'introduit aucune erreur notable, la courbe de dispersion mesurée étant peu différente de celle du chronomètre.

A partir de la courbe de dispersion, il est ensuite aisé d'ajuster le circuit de compensation C_4, R_{12} (Fig. 5) de manière à compenser exactement le retard moyen.

2. *Reproductibilité de fonctionnement du trigger B*

La cellule de mesure est remplacée par un condensateur de 10 μF de grande stabilité, et le courant de polarisation ajusté de manière à réaliser des vitesses de charge de 1, 2 et 4 volts par seconde. On mesure, pour chacune de ces vitesses, les temps correspondant aux potentiels E_x, 0.5-1-1.5-2-2.5 et 3 V. L'analyse de la dispersion des résultats montre que l'écart-type absolu est indépendant du potentiel E_x choisi, avec les valeurs 0.32 millisec (pour 1 V/sec), 0.20 millisec (2 V/sec) et 0.13 millisec (4 V/sec).

Ces valeurs correspondent à des fluctuations du point de basculement d'environ ± 0.3 mV, qui restent dans les limites fixées par le circuit de contrôle associé à la clé B 2.

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3. *Reproductibilité sur le temps de contrôle de surface t_o-t_s*

Les conditions d'expérience sont celles décrites au paragraphe 1, la résistance R 10 étant déconnectée du relais RlA2. Dans ces conditions, le timer fonctionne dès enclenchement de B_1 (instant t_s) et s'interrompt pratiquement au début de la polarisation (instant t_o).

Le temps de formation de la goutte ainsi mesuré présente un écart-type de l'ordre de 0.03%, auquel correspond une reproductibilité de surface d'environ 0.02%.

4. *Précision analytique*

Si la concentration de la substance à doser est suffisante (électro-normalités supérieures à environ $5 \cdot 10^{-4} N$) la différentiation de la relation de *Sand* [1 à 6] permet de prévoir qu'avec l'appareillage décrit, il est possible d'effectuer des dosages affectés d'un écart-type inférieur à 0.2%, si la thermostatisation est assurée à ± 0.1° C et le débit de mercure maintenu constant à mieux de 0.05% (contrôle rigoureux de la hauteur de la colonne et du niveau de la solution).

Une série de mesures systématiques, effectuées avec les ions Pb^{+2}, Cd^{+2}, Zn^{+2}, Ag^{+}, IO_3^{-} dans divers milieux et à des concentrations variables, donnent un écart-type expérimental de cet ordre de grandeur.

En milieu dilué ($C < 10^{-4} N$) il y a avantage à utiliser une nappe de mercure polarisée sous une densité de courant suffisamment faible pour réaliser des temps de transition relativement longs. On réduit ainsi dans une certaine mesure l'interférence due à la capacité de la double couche, qui constitue le facteur primordial limitant la sensibilité de la méthode.

RÉSUMÉ

On décrit un transitomètre de précision, utilisant une électrode à gouttes de mercure de surface contrôlée. L'appareil, entièrement automatisé, permet d'effectuer des dosages rapides, avec une imprécision de l'ordre de 0.2%.

SUMMARY

A detailed description is given of a precision transitometer, which has a dropping mercury electrode with controlled surface. This apparatus, which is completely automatic, allows rapid results, with an error of about 0.2%.

ZUSAMMENFASSUNG

Man beschreibt ein Präzisions-Transitometer, das eine Quecksilbertropfelektrode mit kontrollierter Oberfläche benützt. Dieser vollständig automatisierte Apparat macht schnelle Dosierungen mit einem Fehler von 0.2% möglich.

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A STUDY OF SOME SUBSTITUTED AMIDES OF THIOGLYCOLIC ACID

by

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The present investigation was undertaken for the purpose of developing colored chelating agents that might be applied to the detection or determination of inorganic materials in non-aqueous solutions. The development of reagents which give colored chelates, soluble in non-aqueous solution, would be of value in the detection or determination of inorganic materials especially when combined with extraction procedures.

In this investigation two nitro derivatives of N-(phenyl)-α-mercaptoethanamide (thioanilide) were prepared and studied for possible use as analytical reagents in non-aqueous systems.

The -NH-CO-CH_2-SH grouping is common to both thioanilide and thionalide. The latter was first introduced by BERG *et al.*[1-6] for use as an analytical reagent. ALLAN AND BEAMISH[7] have reported the determination of osmium on a micro scale using thionalide. HOFFMAN *et al.*[8] have also reported the use of thionalide as a precipitant for osmium. The determination of rhodium with thionalide has been reported by KIENITZ AND ROMBOCK[9] and ruthenium has been determined by ROGERS, BEAMISH AND RUSSELL[10]. BERSIN[11] reported using thioanilide as a reagent for cobalt.

WEISS[12] has reported the preparation of N-(4-nitrophenyl)-α-mercaptoethanamide and N-(3-nitrophenyl)-α-mercaptoethanamide and their gold salts. However, no general analytical study was made by WEISS.

Apparatus

A Beckman Model DK recording spectrophotometer was used to obtain absorption curves. The solutions were contained in 1.00 cm silica cells.

All spectrophotometric measurements at a specified wavelength were made on a Beckman Model B spectrophotometer using 1.00 cm Corex cells.

Reagents and solutions

Aniline. The commercial product was purified by distillation.

α-Naphthylamine. The commercial product was purified by recrystallization from warm petroleum ether, Grade B.

All other amines used were Eastman White Label.

α-Mercapto-N-2-naphthylacetamide, Eastman White Label.

All other chemicals used were of analytical reagent grade.

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EXPERIMENTAL

A. Preparations

The two nitro derivatives of thioanilide, N-(3-nitrophenyl)-α-mercaptoethanamide and N-(4-nitrophenyl)-α-mercaptoethanamide, were prepared by the method reported by Weiss[12]. The yields were 9% and 15% respectively.

Attempts to make the following compounds were unsuccessful: N-(1-phenylazo-2-naphthyl)-α-mercaptoethanamide, N- [1-(1-naphthylazo)-2-naphthyl]-α-mercaptoethanamide, N-(4-phenylazophenyl)-α-mercaptoethanamide, and N-(2-nitrophenyl)-α-mercaptoethanamide.

B. Procedure and results

The following procedure was used to determine with which ions the reagents react. Each ion was tested in acidic, neutral, and basic media. To 1 drop of test solution, which contained 5 mg ion/ml, 5 drops of water were added and the pH adjusted to about 2, 7 or 10. To this, 10 drops of the reagent (0.05% in ethanol) were added and then it was noted whether or not precipitation occurred. The formation of a precipitate generally indicated that a reaction had taken place while a cloudiness usually resulted when the reagent alone separated from solution. The pertinent data are shown in Table I.

TABLE I

COLOR OF PRECIPITATES FORMED

Ion	*N-(3-nitrophenyl)-α-mercaptoethanamide*	*N-(4-nitrophenyl)-α-mercaptoethanamide*	*Thioanilide*
Copper (II)			
acidic	blue	blue	yellow
neutral	blue	NAR*	yellow
basic	blue	NAR	yellow
Gold (III)			
acidic	white	NAR	flesh
neutral	white	brown	flesh
basic	white	NAR	white
Silver			
acidic	yellow	yellow	yellow
basic	yellow	yellow	yellow
Cadmium			
acidic	white	NAR	white
neutral	NAR	NAR	white
basic	NAR	NAR	white
Mercury (I)			
acidic	NAR	yellow	NAR
Mercury (II)			
acidic	white	yellow	white
Thallium (I)			
neutral	yellow	yellow	yellow
basic	yellow	yellow	yellow
Tin (II)			
acidic	white	NAR	white
Tin (IV)			
acidic	white	NAR	white
Lead			
acidic	NAR	NAR	yellow
neutral	yellow	NAR	yellow
basic	yellow	NAR	yellow
Bismuth (III)			
acidic	yellow	NAR	yellow
Arsenic (III)			
acidic	white	NAR	NAR
neutral	white	NAR	white
basic	NAR	NAR	white

---

* No apparent reaction.

TABLE I (continued)

Ion	*N-(3-nitrophenyl)-α-mercaptoethanamide*	*N-(4-nitrophenyl)-α-mercaptoethanamide*	*Thioanilide*
Antimony (III)			
acidic	white	yellow	white
Nickel			
neutral	brown	NAR	brown
basic	brown	NAR	brown
Cobalt (II)			
neutral	red-brown	brown	red-brown
basic	red-brown	brown	red-brown
Palladium (II)			
acidic	orange	NAR	orange
neutral	orange	red-orange	orange
basic	yellow	red-orange	orange
Platinum (IV)			
neutral	NAR	red-brown	white
basic	NAR	red-brown	white
Manganese (II)			
neutral	NAR	NAR	white
basic	NAR	NAR	white
Iron (II)			
neutral	NAR	NAR	purple solution
basic	NAR	NAR	purple solution
Iron (III)			
acidic	NAR	NAR	white
neutral	NAR	NAR	olive-tan
basic	NAR	NAR	olive-tan
Ruthenium (III)			
neutral	NAR	NAR	brown
basic	NAR	NAR	brown

In cases where precipitation occurred, the systems were extracted with an organic solvent to determine if the precipitate was soluble in the solvent used. The solvent in most cases was *n*-butyl acetate.

A study of the extraction of the N-(3-nitrophenyl)-α-mercaptoethanamide complex of cadmium was made. Since cadmium reacts in acidic solution and zinc does not, it was believed that this might afford a very good method of separating cadmium and zinc. However, it was found that what at first appeared to be an excellent extraction was actually a shift of equilibrium and the reagent alone was extracted. The cadmium was determined polarographically.

A study of the extraction of the N-(3-nitrophenyl)-α-mercaptoethanamide complex of cobalt from ammoniacal solutions was also made. Using *n*-butyl acetate as a solvent, it was found that the results were neither reproducible nor quantitative. *n*-Butyl alcohol, methyl isopropyl ketone, mixtures of *n*-butyl acetate and *n*-butyl alcohol, *n*-butyl acetate and isopropyl ketone, *n*-butyl alcohol and methyl isopropyl ketone were also used, but the extraction was not satisfactory in any case.

A study of reactions in non-aqueous media was also made using a selected number of ions. This was done by first extracting the ion into a suitable non-aqueous solvent, then adding the reagent to the non-aqueous phase. The criterion of a reaction taking place was a change in the absorption of the solution. It was found that these reactions did not offer any convenient method of analysis. These data are shown in Table II.

DISCUSSION

Coordination of metals with the Ar-NH-CO-CH_2-SH grouping can possibly occur through the -NH-, -CO-, or the -OH groups.

TABLE II

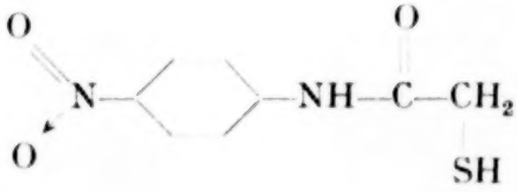
REACTIONS IN NON-AQUEOUS MEDIA

Ion	*Addenda and solvent*	*N-(3-nitrophenyl)-α-mercaptoethanamide*	*N-(4-nitrophenyl)-α-mercaptoethanamide*
Cu (II)	NCS^- in BuOH*	none	none
Hg (II)	I^- in BuOH	none	none
Pb	I^- in MIK**	none	none
Ni	$NCS^- + NH_3$ in BuOH	dark yellow	olive brown
Co (II)	$NCS^- + NH_3$ in BuOH	brown	tan
Pd (II)	$NCS^- + NH_3$ in BuOH	yellow	yellow
Au (III)	Cl^- in BuOH	none	none

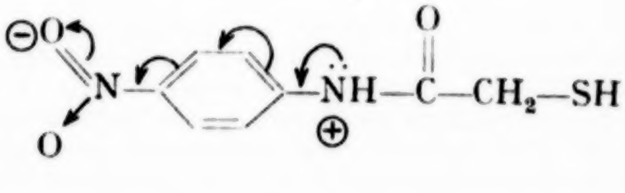
* *n*-Butyl alcohol
** Methyl isopropyl ketone

Because nitrogen is a much stronger electron donor than oxygen, the authors believe that coordination through the -NH- is predominate.

Consider a molecule of the type



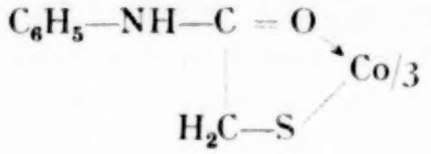
The nitro group is electron withdrawing because of inductive and resonance effects. In the case of the para derivative, it would be expected that the nitro group would deactivate the amide nitrogen. This may be represented by:



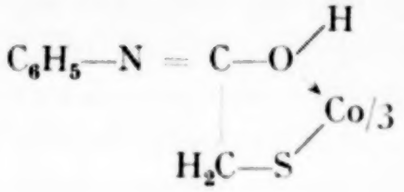
From the above one would expect the nitro group to decrease the reactivity of the reagent, especially if coordination takes place through the -NH- group. Since the nitro group is far removed from the -NH-, the inductive effect should not be too important, but it would also add to the resonance effect.

If the nitro group is oriented meta to the -NH- group, then the resonance effects are virtually eliminated and the inductive effect is the main factor to be considered. One would expect the inductive effect to decrease the reactivity of the reagent, but not as much as the resonance effect does in the *para* compound. These expectations are substantiated by the fact that the *meta* derivative reacts with 15 metal ions and the *para* derivative reacts with 10 metal ions. Thionalide reacts with 20 metal ions. Thioanilide also reacts with 20 ions as reported in Table I.

Bersin has reported that the reaction of thioglycolamide with cobalt yields a red-brown salt that corresponds to structure I or II.

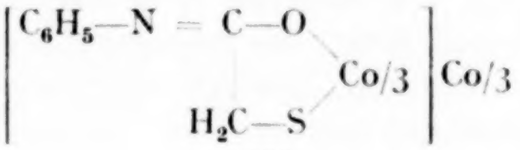


I



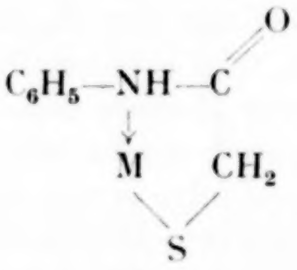
II

and a brown salt that corresponds to structure III.



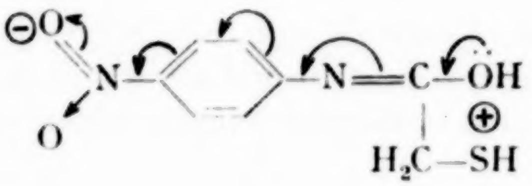
III

The authors believe that structure I can be ruled out because substitution of a nitro group in the *para* position would not affect this type of complex formation. Since the effect is pronounced, the authors believe that the coordination takes place through the amide nitrogen as shown in structure IV.



IV

However, this does not rule out the possibility of coordination as depicted in structure II since the resonance effect can be represented by:



and in this case the reactivity will also be reduced.

After finding with which ions N-(3-nitrophenyl)-*α*-mercaptoethanamide reacts, it was then decided to study some of the reactions more thoroughly.

A more detailed study was made of the cadmium extraction since cadmium reacted with N-(3-nitrophenyl)-*α*-mercaptoethanamide in acidic solution to form a white precipitate while zinc did not react. This appeared to be an ideal method of separating cadmium and zinc. However, when a quantitative study of the reaction was made, it was found that the cadmium remained in the aqueous phase. The reagent is most likely extracted, thus causing a shift in equilibrium, and mere extraction of the reagent is all that is realized.

The extraction of the cobalt complex of N-(3-nitrophenyl)-*α*-mercaptoethanamide appeared to be suitable for small amounts of cobalt. However, when solutions of the same concentration were extracted and the optical density of the extract read at 480 mμ (which is the absorption peak for the complex), it was found not to be reproducible. At first the difficulty was attributed to slight differences in pH, but even after buffering the solution, the reproductibility was not improved. The efficiency of the extraction was also determined, and it was found that it varied between 8 and 37%. In determining the efficiency of the extraction, the cobalt was determined by the thiocyanate-acetone method and also with nitroso-R-salt. These methods were used to determine how much cobalt was left in the aqueous phase after extraction.

The color of the complex was observed to be very intense in an ammoniacal solution. Qualitatively one may detect one microgram of cobalt per drop easily with the reagent. In such concentrations, however, the test solution is a brown to tan color and a precipitate does not form.

It was then decided to try to determine the cobalt after extraction into a non-aqueous solvent. The cobalt thiocyanate complex was extracted into amyl acetate and the reagent added. It was found that there was no color development if ammonia was not present and the presence of ammonia decreased the percentage extraction considerably. Ethylenediamine was tried in place of ammonia but it was not satisfactory.

From this study, it can be concluded that the Ar-NH-CO-CH_2-SH structure offers promise as an analytical reagent. This is especially true of the compounds in which Ar- contains a chromophoric group. A more detailed study of different Ar-groups might lead to some very interesting results relating to selectivity.

It was found that substitution of nitro groups into the aromatic nucleus made the reagent more selective than the parent compound. This might also be accomplished by the introduction of groups which would sterically hinder the reactive site, thus decreasing reactivity. In general, the sensitivity of the nitro derivatives was less than that of the parent compound, although they were more stable toward oxidation. The nitro derivatives are soluble in alcohol, ether, and various esters, and insoluble in water.

The greatest advantage of carrying out color reactions in non-aqueous solvents is the elimination of interferences. A second advantage is the fact that the colored substance can be determined in the non-aqueous phase directly without reverting to an aqueous phase.

ACKNOWLEDGEMENT

The authors acknowledge the aid of the Office of Ordnance Research, U.S. Army, under whose program this research was conducted.

SUMMARY

Coordination of metals with the group -NH-CO-CH_2-SH can possibly occur through the -NH-, -CO- or enolic -OH. Some studies have been made in an attempt to learn more of the nature of such reactions and so establish the most promising course for developing new reagents having this type of reacting group.

RÉSUMÉ

La coordination des cations avec le groupement, -NH-CO-CH_2-SH, peut se faire sur les fonctions -NH-, -CO- ou -OH énolique. Des recherches ont été effectuées pour essayer de mieux connaître la nature de telles réactions et, de cette manière, établir la meilleure manière de développement de nouveaux réactifs possédant ce type de groupement.

ZUSAMMENFASSUNG

Die Koordination der Kationen mit der -NH-CO-CH_2-SH-Gruppe kann an der -NH-, der -CO- oder der enolischen -OH-Gruppe stattfinden. Die hier beschriebenen Untersuchungen wurden ausgeführt, um die Natur solcher Reaktionen besser kennen zu lernen und den besten Weg zur Entwicklung neuer Reagenzien, die eine derartige Gruppe enthalten, zu finden.

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VOLUMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS

IX. REDUCTION WITH FERROUS ETHYLENEDIAMINE SULPHATE SODIUM METAVANADATE METHOD

by

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Ferrous ethylenediamine sulphate, $FeSO_4$ $(CH_2.NH_3)_2$ SO_4. $4H_2O$, reacts with sodium metavanadate in acid medium according to the following equation:

$$VO_3^- + Fe^{+2} + 4H^+ = VO^{+2} + Fe^{+3} + 2\ H_2O$$

B. Singh *et al.*[1] have used ferrous ethylenediamine sulphate for the indirect volumetric estimations of potassium bromate, potassium metaperiodate, potassium dichromate, potassium ferricyanide, potassium permanganate, potassium persulphate, hydrogen peroxide, ceric sulphate and sodium meta-vanadate. The excess of ferrous ethylenediamine sulphate added to each of the substances was titrated with standard potassium permanganate, potassium dichromate and ceric sulphate. In the present investigation the substances have been determined indirectly by a volumetric method using ferrous ethylenediamine sulphate as reducing agent. The excess of standard ferrous ethylenediamine sulphate solution added to each of the substances was titrated with standard sodium metavanadate solution using diphenylbenzidine as an indicator.

EXPERIMENTAL

A known amount of each substance was transferred to a conical flask and 20 ml of water, 20 ml of phosphoric acid mixture and a known excess (20 ml) of standard 0.05*N* ferrous ethylenediamine sulphate solution were added to it. In case of potassium ferricyanide, 5 ml of freshly prepared solution of ferric chloride[2] (containing 1.0 g per 100 ml), 20 ml of 1*N* HCl, 30 ml of water and 20 ml of 0.05*N* ferrous ethylenediamine sulphate solution were added. The precipitate of $Fe_3[Fe(CN)_6]_2$ formed, was filtered and thoroughly washed with water. The filtrate, containing the excess of ferrous ethylenediamine sulphate, was acidified with phosphoric acid mixture. In each case the excess of ferrous ethylenediamine sulphate was titrated against 0.05*N* sodium metavanadate solution using diphenylbenzidine as indicator. Necessary indicator correction was made in these titrations.

From the amount of sodium metavanadate used in each titration, the amount of ferrous ethylenediamine sulphate required for the reduction of each substance, and consequently the amount of each substance was determined. The results showed that 0.348-0.952 meq. of the substances listed above can be determined indirectly by the volumetric method, using ferrous ethylenediamine sulphate as reducing agent in acid medium.

Phosphoric acid mixture was prepared by mixing 75 ml H_2SO_4 (sp.gr. 1.84) with 75 ml H_3PO_4 (sp.gr. 1.75) and diluting it to 500 ml with water. All chemicals except ceric sulphate, used in this investigation were of guaranteed purity. Ceric sulphate was standardized with ferrous ethylenediamine sulphate which was prepared by the method of CARAWAY AND OESPER[3].

SUMMARY

Ferrous ethylenediamine sulphate has been used as a reducing agent in acid medium for the indirect volumetric determinations of potassium bromate, metaperiodate, dichromate, ferricyanide, permanganate and persulphate and of hydrogen peroxide, ceric sulphate and sodium metavanadate. The excess of standard solution of the reagent added to each of the substances was titrated with standard sodium metavanadate solution using diphenylbenzidine as an indicator.

RÉSUMÉ

Le sulfate double de fer(II) et d'éthylènediamine a été utilisé comme réducteur, en milieu acide, pour les dosages volumétriques indirects du bromate, du métaperiodate, du dichromate, du ferricyanure, du permanganate et du persulfate de potassium, du peroxyde d'hydrogène, du sulfate de cérium(IV) et du métavanadate de sodium. L'excès de la solution étalon du réactif, ajoutée à chacune de ces substances, est titré par une solution étalon de métavanadate de sodium, en présence de diphénylbenzidine comme indicateur.

ZUSAMMENFASSUNG

Eisen(II)-Äthylendiaminsulphat wurde als Reduktionsmittel in saurer Lösung zur indirekten volumetrischen Bestimmung von Kaliumbromat, -metaperjodat, -dichromat, -ferricyanid, -permanganat und -persulphat und von Wasserstoffperoxyd, Cer(IV)-sulphat und Natriummetavanadat verwendet. Der zu jeder dieser Substanzen zugefügte Überschuss an Titerflüssigkeit wurde mit einer Titer-Natriummetavanadatlösung in Gegenwart von Diphenylbenzidin als Indikator zurücktitriert.

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ON THE SEMIMICRO DETERMINATION OF METHOXYL

by

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The conventional method for determination of methoxyl groups according to Zeisel[1] and modified by Vieböck and Schwappach[2] or Vieböck and Brecher[3] has proved to be safe and reliable and is almost the only method used. Although no fundamental changes have been made, there has been much discussion of details and many papers have been published proposing various improvements to applications of the method to an increasing number of substances.

The methoxyl determination is a very useful tool in studying the chemistry of wood and lignin and has been routine at this laboratory for many years. Much work has been done on collating the literature and in finding the best procedure for carrying out this analysis. Many of our findings were quite in accordance with the excellent examination of the method recently published by Belcher, Fildes and Nutten[4]. However, on some points our results differ and it seemed worth while to publish our results on these points and discuss them further.

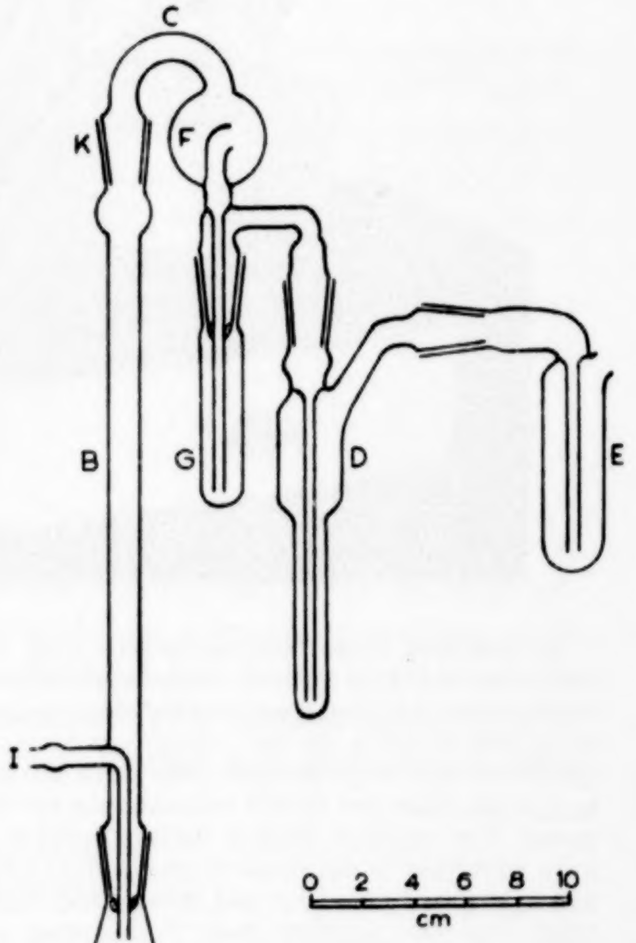

Fig. 1. Apparatus for the determination of methoxyl.

Apparatus

The apparatus described by Gran[5] has been used at this laboratory for some time. It has many advantages. The design of the washers and receivers is such that it is not necessary to dismount the apparatus after each analysis, and the inner tube of the bubblers are sealed to the lower end of the male joint to get a rugged unit, easy to wash and repair. However, it was found unnecessary to use double washers and receivers, and the watercooling could also be omitted.

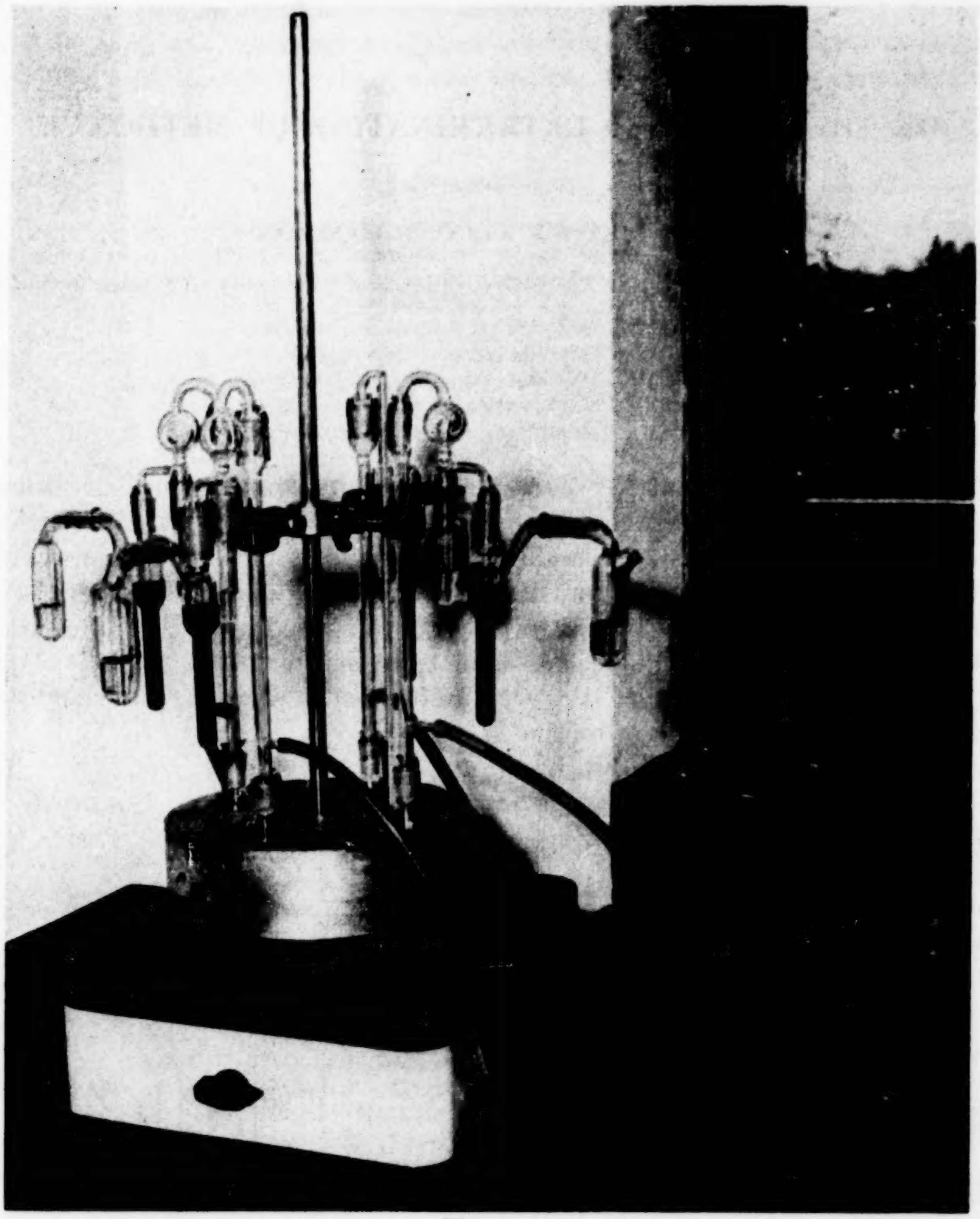

Fig. 2.

In designing a modified apparatus (Fig. 1) the advantages of the apparatus according to GRAN were retained. It is entirely made of borosilicate glass, using standard tapered ground joints B 14 throughout. All joints are secured with metal springs. The reaction flask A is an ordinary conical flask and the inlet for the carrier gas is drawn through the wall of the condenser and sealed to the lower end of its ground joint. The advantage of this arrangement is that the rubber tubing to the gas inlet can be left mounted on the tube I, so that shifting of the reaction flasks become faster. The reaction flask is flatbottomed to make it easier to weigh. The air condenser B is the only part that is mounted to the stand. The clamp used for this is so made that the apparatus can easily be moved up and down. The bulb F is constructed to prevent wash solution sucking back into the reaction flask if bumping eventually occurs. (Wood samples sometimes cause bumbing.) The receiver D contains 10 ml, which has proved sufficient, and is more easily emptied than the double bubbler previously used. If the apparatus is operated outside of the hood, it is necessary to eliminate the bromine vapors that leave the receiver. To effect this, the bubbler E has been introduced. It is filled with sodium hydroxide or any other good absorbent for bromine. The joint K is useful when the apparatus is cleaned.

The method of heating the reaction flask seems to be rather non-critical, so the earlier recommended oil bath has been substituted by an aluminium block with drilled holes, 40 mm wide and 40 mm deep. The block is placed on a hot plate and heated to 140°-160° C. By using a large block, 70 mm thick and with a diameter of 240 mm, with four holes and a stand in the middle, threaded into the block, an easy handled unit is obtained which requires a minimum of space (see Fig. 2). The carrier gas is taken from a carbon dioxide cylinder provided with four separately regulated needle valves.

In routine, four determinations are carried out at the same time. Usually the apparatus needs rinsing only once a day.

The apparatus is obtainable from the firm Werner-Glas, Slöjdgatan 1, Stockholm C.

Solution of sample

In many cases it is desirable to add to the hydriodic acid some substance to facilitate the solution of the sample. Phenol and acetic or propionic acid or their anhydrides seem to be the most popular reagents for this purpose. BELCHER *et al.*[4] recommend the mixture of phenol and propionic anhydride proposed by ELEK[6]. This mixture was compared with the mixture described by KIRSTEN[7]. Both mixtures were equally satisfactory in dissolving the samples tested, but the latter one had the advantage of constituting only one phase when mixed with the hydriodic acid both in the cold and at the boiling point, and can thus be added in one portion together with the hydriodic acid.

Wash liquids, sulfur-free substances

The purpose of washing the gas before introducing it into the receiver is to remove traces of hydriodic acid and iodine. The wash solution must not retain methyl iodide. Of the great variety of solutions proposed, only those containing sodium thiosulfate seem to be unsatisfactory[8,9]. In the apparatus just described, no iodine is carried over when a reasonable gas speed is used, so the only substance to remove is hydrogen iodide and for this purpose distilled water, dilute hydrochloric acid, solutions of sodium bicarbonate, cadmium sulfate or sodium antimony tartrate proved to work equally well (see Table I). Thus, as far as work with sulfur-free substances is concerned, the choice of wash solution is rather non-critical.

Wash liquids, sulfur-containing substances

When inorganic compounds containing sulfur are boiled with hydriodic acid, hydrogen sulfide is formed in most cases. Even some organic compounds, *i.e.* thioacetamide and some disulfides give hydrogen sulfide. When samples containing such substances are analysed, low results are often obtained if ordinary wash solutions are used. Formation of mercaptans has been mentioned as a possible source of error already by ZEISEL[10] and KIRPAL AND BÜHN[11]. This reaction may proceed according to

$$\mathrm{CH_3I + H_2S \rightleftharpoons CH_3SH + HI}$$
$$\mathrm{CH_3SH + CH_3I \rightleftharpoons CH_3SCH_3 + HI}$$

These reactions will have a greater tendency to proceed to the right the higher the pH value of the wash solution. Therefore alkaline solutions should be avoided. This is also indicated by the values obtained by GRAN[12] which show very low and irregular yields when sodium bicarbonate was used as wash solution. Compare also Table I,

TABLE I

INFLUENCE OF DIFFERENT WASH SOLUTIONS

Vanillin was used as test substance in all cases.

a. water as wash solution				
Sample weight, mg:	30.48	29.63	32.27	32.28
Na_2SO_4 weight, mg:	0	21.0	30.8	60.4
Yield, %	100.5	101.2	100.5*	100.1*
b. 5% sodium bicarbonate as wash solution				
Sample weight, mg:	30.51	30.99	30.88	30.49
Na_2SO_4 weight, mg:	0	20.4	30.0	61.4
Yield, %	100.4	97.7	99.7	96.9*
c. 10% sodium antimony tartrate as wash solution				
Sample weight, mg:	29.46	29.12	26.1	30.58
Na_2SO_4 weight, mg:	0	29.2	50.0	59.9
Yield, %	100.3	99.9	95.1	95.9
d. 1N hydrochloric acid as wash solution				
Sample weight, mg:	30.17	30.88	31.51	31.57
Na_2SO_4 weight, mg:	0	20.9	30.0	59.3
Yield, %	100.3	99.9	100.2	99.5*
e. 5% cadmium sulfate as wash solution				
Sample weight, mg:	35.86	39.24	33.26	34.49
Na_2SO_4 weight, mg:	0	20.5	30.0	58.9
Yield, %	100.5	100.5	100.3	100.1

* Bromine in receiver bleached.

which shows methoxyl yields in per cent of theoretical, when different wash solutions are used. Sodium sulfate was added as indicated.

Another source of error may be the reaction of hydrogen sulfide with the bromine in the receiver. In many cases a considerable bleaching of the absorption solution has been noticed, and BELCHER *et al.*[4] showed, that when further bromine was added to the receiver the yields became satisfactory.

The requirements that should be put on a wash solution are thus: 1) it shall absorb hydrogen iodide, 2) it shall absorb hydrogen sulfide, to prevent it reaching the receiver, 3) it shall not absorb methyl iodide, that is also, it shall not be alkaline and must not contain thiosulfates. Among several wash solutions proposed (red phosphorus in distilled water, sodium bicarbonate and iodine solution) GRAN[12] finds that cadmium sulfate is the best. BELCHER *et al.*[4], however, recommend sodium antimony tartrate[13], as described by FRANZEN, HEGEMANN AND DISSE[14]. When the two solutions were compared (Table I) using rather large quantities of sodium sulfate in the reaction flask, the cadmium sulfate solution gave the best results. It could be shown that the absorption of hydrogen sulfate was not complete when the wash liquid of FRANZEN *et al.* was used. When small amounts of sodium sulfate were used both solutions were satisfactory, but the cadmium sulfate solution gave a precipitate that was easier to remove when cleaning the apparatus.

References p. 283

SUMMARY

Various steps in the semimicro determination of methoxyl are discussed. An improved design of apparatus is described and different compositions of the hydriodic acid and the wash solutions are compared.

RÉSUMÉ

Les différentes phases du sémimicrodosage du groupement méthoxyle sont examinées. Un modèle perfectionné de l'appareil est décrit et différentes compositions des solutions d'acide iodhydrique et de lavage sont comparées.

ZUSAMMENFASSUNG

Verschiedene Stufen der Semimikro-Methoxyl-Bestimmung werden erörtert. Eine verbesserte Apparatur wird beschrieben und verschiedene Zusammensetzungen der Jodwasserstoffsäure- und Waschlösungen werden verglichen.

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REACTIONS OF ORGANIC BASES WITH BORON TRIBROMIDE IN NON-AQUEOUS SOLVENTS

by

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INTRODUCTION

The technique of acid base titrimetry in organic analysis has been shown in many cases to be best suited to non-aqueous solvents[1,2,3]. The solvent system thionyl chloride was selected as a working non-aqueous medium in which organic base reactions might be carried out. Boron tribromide was used as the titrant for the various organic compounds dissolved in the thionyl chloride.

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[*] Based upon a thesis submitted by MALCOLM C. HENRY to the Faculty of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

EXPERIMENTAL

Materials. Thionyl chloride, *iso*quinoline, 2-methyl-5-ethylpyridine and β-picoline were prepared and stored in a manner similar to that described in a previous article[4]. Acridine was recrystallized from ethyl alcohol, filtered and dried in a vacuum desiccator over phosphorous pentoxide.

Procedure. The conductance cell and techniques for conductometric titrations were similar to those discussed in a previous article. Solid reagents were weighed on an analytical balance and added directly to the conductance cell. Mixed titrations were carried out by dissolving known amounts of the selected bases in the thionyl chloride solvent.

RESULTS

Organic bases usually react with boron tribromide in a 1:1 molar ratio. In the case of *iso*quinoline an apparent anomaly occurs. If boron tribromide is added to excess *iso*quinoline, a reaction occurs that indicates a molar ratio of *iso*quinoline to boron tribromide of 3:1. If *iso*quinoline is added to excess boron tribromide, the normal 1:1 addition compound is formed. These compounds have been isolated from benzene solution and analysed. The 1:1 addition compound is a white crystalline compound and the 3:1 addition compound is a deep colored complex. Conductometric titrations lend further support to the analyses.

Fig. 1 shows the titration of *iso*quinoline dissolved in thionyl chloride with boron tribromide. The first break in the curve corresponds to the formation of a compound at a ratio of 3:1 *iso*quinoline to boron tribromide. Beyond this break the initial addition compound appears to be breaking down to the more stable 1:1 addition compound. Addition of more boron tribromide caused the conductance to rise rapidly.

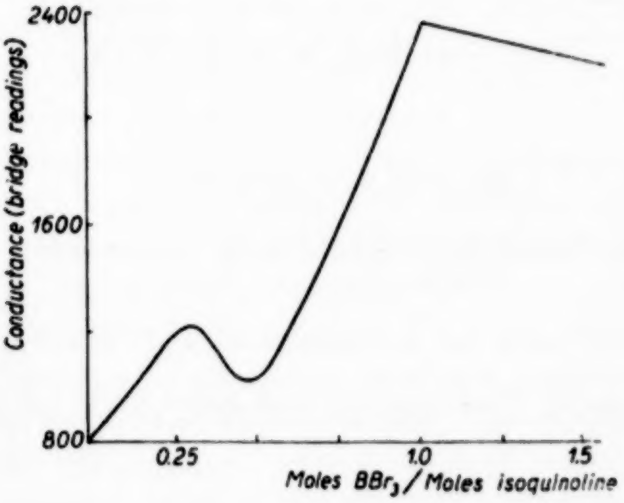

Fig. 1. Conductometric titration of *iso*quinoline with boron tribromide.

The conductance reached a limiting value at the molecular ratio of a 1:1 addition compound between the *iso*quinoline and the boron tribromide. Beyond this point the conductance gradually decreased due to the decreasing dielectric of the solution with subsequent lessening of the ionization. The reaction sequence may be visualized by the following reactions:

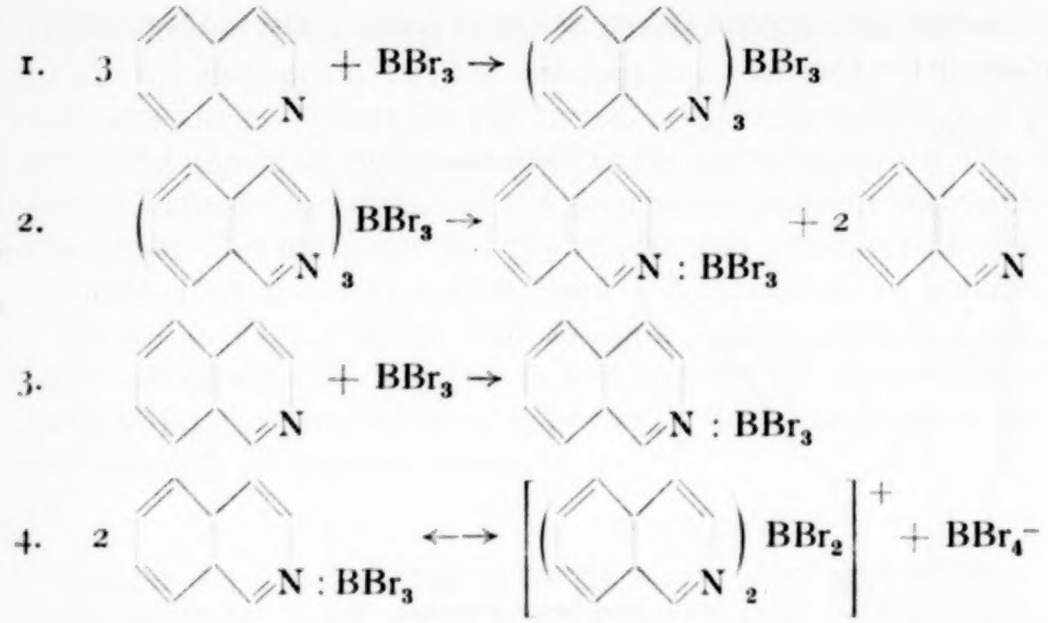
1. 3 + BBr3 → ( )3 BBr3
2. ( )3 BBr3 → N : BBr3 + 2
3. + BBr3 → N : BBr3
4. 2 N : BBr3 ←→ [( )2 BBr2]+ + BBr4−

Fig. 2 is the result of the titration of 4.3 millimoles of *iso*quinoline and 2.3 millimoles of quinoline dissolved in 25 ml of thionyl chloride with boron tribromide. As the boron tribromide was added, the *iso*quinoline boron tribromide 3:1 compound formed first as represented by point *a*. Further addition of boron tribromide caused the occurrence of a second peak resulting from the addition compound formed between the quinoline and boron tribromide. This peak is presumably a result of two competing reactions namely, the ionization of the quinoline addition compound and the decrease in conductance as the anomalous *iso*quinoline complex slowly rearranges to the 1:1 addition compound. The dotted line suggests the course of the probable rearrangement similar to Fig. 1. Point *b* indicates the stoichiometric end-point for the titration of the quinoline. The rising portion of the curve beyond point *b* is due to the formation of the more stable 1:1 addition compound with *iso*quinoline. Point *c* indicates the neutralization of the total *iso*quinoline added. Maximum conductance is noted due to the ionization of the newly formed salt.

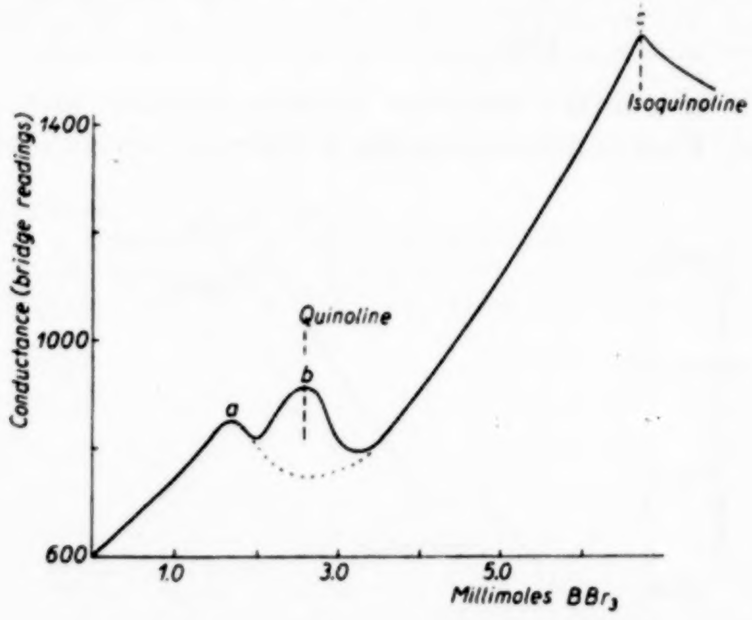

Fig. 2. Conductometric titration of quinoline and *iso*quinoline with boron tribromide.

The falling off of the conductance beyond the equivalence point is due to the decreasing dielectric as explained for Fig. 1.

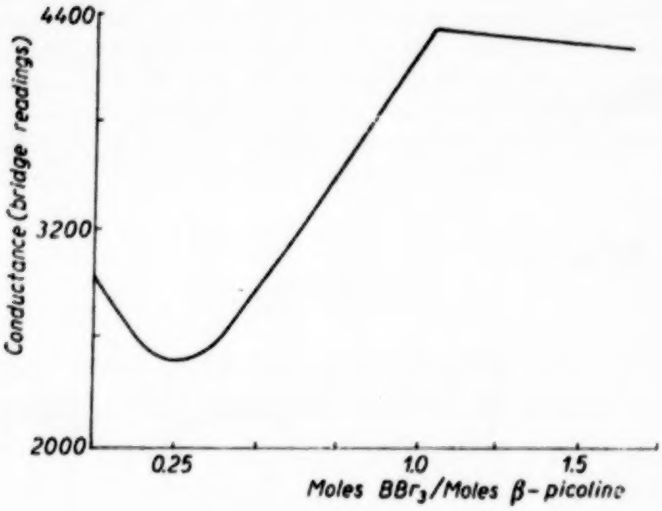

Fig. 3. Conductometric titration of β-picoline with boron tribromide.

Fig. 3 shows the conductometric titration of 3-picoline dissolved in thionyl chloride with boron tribromide. The initial rapid decrease in conductance is experimentally reproducible but as yet unexplained. The subsequent rise in conductance is due to the formation of a 1:1 addition compound. This neutralization results in ionization of the salt molecule with increased conductance as more and more salt is formed. The conductance reaches a limiting value at the end-point as a result of complete neutralization. The plateau beyond the end-point indicates no further reaction. The reaction is tabulated as follows:

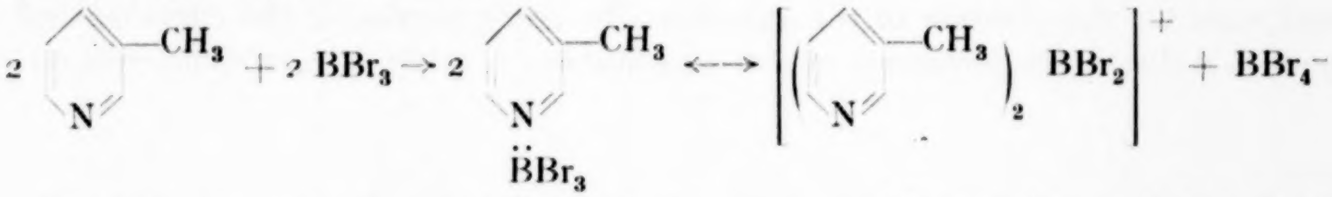

Fig. 4 is the result of a mixed titration between pyridine and 2-methyl-5-ethylpyridine (aldehydine). Four millimoles of the substitute pyridine and 6.0 millimoles

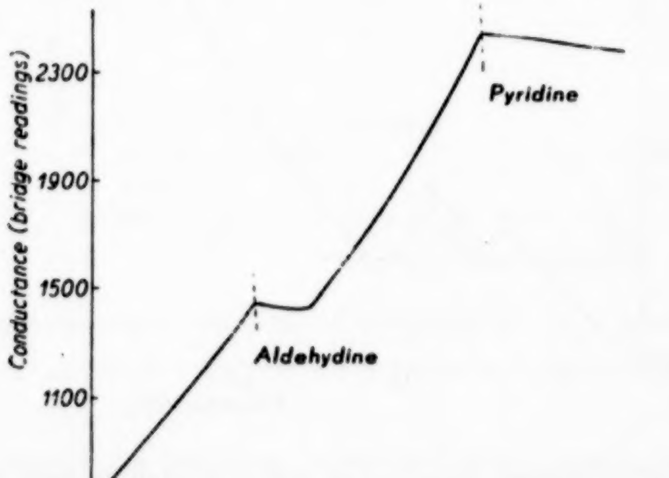

Fig. 4. Conductometric titration of aldehydine and pyridine with boron tribromide.

of pyridine were dissolved in 25 ml of thionyl chloride. Boron tribromide was added in known increments and the conductance measured. The first break in the curve indicates the end-point for the titration with the substituted pyridine. The second end-point shows the neutralization of the added pyridine. The rising portions of the curves indicate formation of the respective addition compounds with subsequent ionization. This indicates that the substituted pyridine is the stronger base in thionyl chloride. This probably results from a combination of inductive and steric effects.

Curves in Figs. 2 and 4 indicate that certain organic bases in thionyl chloride have sufficient basic character to be titrated with boron tribromide. These reactions have interesting implications concerning the estimation of the concentration and the strength of organic bases.

SUMMARY

Conductometric titration curves are presented for the reaction of several organic bases with boron tribromide in the acidic solvent thionyl chloride. Organic bases in thionyl chloride are shown to exhibit electrogenic strength suitable for stoichiometric titrations with boron tribromide. Several curves are presented that illustrate the difference in base strength suitable for mixed titrations. Use may be made of this technique for organic acid base titrimetry.

RÉSUMÉ

Des courbes de titrage conductométrique sont présentées pour la réaction de plusieurs bases organiques avec le tribromure de bore, en solution dans le chlorure de thionyle. Ces bases organiques peuvent ainsi être titrées stoechiométriquement par le tribromure de bore. Plusieurs courbes sont données pour des titrages de mélanges. Cette technique peut être utilisée pour l'analyse titrimétrique des acides et des bases organiques.

ZUSAMMENFASSUNG

Die Kurven, welche man bei der konduktimetrischen Titration verschiedener organischer Basen mit Bortribromid in Thionylchloridlösung erhält, werden beschrieben. Es wird gezeigt, dass die organischen Basen dann stöchiometrisch mit dem Bortribromid reagieren. Auch die Titrationskurven von Gemischen von Basen verschiedener Stärke werden angeführt. Diese Arbeitstechnik kann in der organischen Säure-Basen-Titrimetrie angewendet werden.

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THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM BY MEANS OF THE AZIDE ION*

by

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INTRODUCTION

Univalent anions derived from halogenoids or pseudohalogens possess striking similarities both to the halogens and to themselves[1]. Two such halogenoid anions are the thiocyanate ion and the azide ion, both of which have the same electronic

$$[:\ddot{S}:\,:C:\,:\ddot{N}:]^{-} \quad [:\ddot{N}:\,:N:\,:\ddot{N}:]^{-}$$

structure[2]. Not only are their electronic structures similar but their chemical behavior with such ions as ferric, lead, silver, and thallous are closely parallel. As it is well known that thiocyanate produces a yellow color with uranium(VI), it was hoped that azide might react in a similar fashion and that the color produced might be utilized for the quantitative determination of uranium. Tests showed that a yellow is produced the intensity of which is proportional to the concentration of uranium.

The absorbancy of a solution containing 1 mg uranium per 25 ml under comparable conditions of wavelength (375 mμ) is 0.750 for the uranium-azide system, 0.620 for the uranium-thiocyanate system in 3:2 acetone:water[3], and 0.840 for uranium-thiocyanate in ethyl acetate-acetone-water[4]. The molar absorbancy index, a_M, $\left(\frac{\text{absorbancy}}{\text{cell length} \times \text{concentration}}\right.$, where cell length in these systems is in centimeters and concentration is in moles per liter) is 4450, 3690, and 5000, respectively. At 360 mμ, however, the molar absorbancy index of the uranium-azide system is 5300. Hence, the uranium-azide reaction is more sensitive than the uranium-thiocyanate reaction in acetone-water but not as sensitive as the uranium-thiocyanate reaction in ethyl acetate-acetone-water at 375 mμ. Furthermore, an aqueous solution of the azide reagent is used which is considerably more stable than the acetone solution of thiocyanate usually employed. Another advantage of the azide method is the greater stability of the colored product.

Because of the interest in uranium analysis at this time, this report is being issued to encourage further investigations with this reagent.

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* Publication authorized by the Director, U. S. Geological Survey.

EXPERIMENTAL DATA

Spectrum of uranyl azide complex

The absorption spectrum of the uranyl azide system was determined on a solution (25 ml total volume) containing 1 mg uranium, 5 ml of 7 percent HNO_3, and 20 ml of 3 molar sodium azide, with water as reference, using a recording spectrophotometer. There is an increase in absorbancy as the wavelength decreases from 530 mμ (Fig. 1). For further work a wavelength of 360 mμ was chosen because this gives good sensitivity.

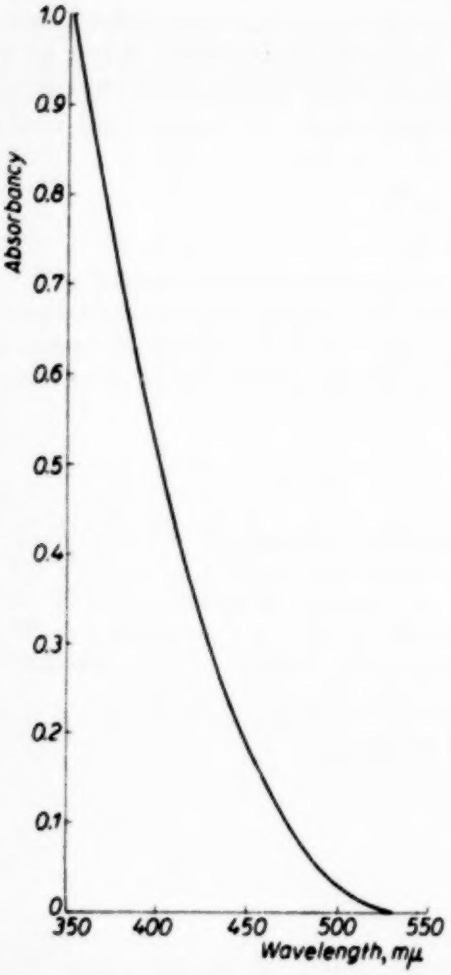

Fig. 1. Spectrum of uranyl azide.

Concentration of azide

The absorbancy of a solution (25 ml total volume) containing 0, 0.1, and 1 mg uranium and 5 ml of 7 percent HNO_3 varies with azide concentration (Table I).

TABLE I

ABSORBANCY AS A FUNCTION OF AZIDE CONCENTRATION

Each solution contains 5 ml of 7 percent HNO_3 per 25 ml. γ = 360 mμ, slit width = 0.10 mm, 1 cm silica cells, reference water.

U *mg*	*3 molar NaN_3 ml*	*Absorbancy*
0	5	0.017
0	10	0.020
0	15	0.020
0	20	0.032
0.1	5	0.091
0.1	10	0.098
0.1	15	0.103
0.1	20	0.111
1.0	5	0.748
1.0	10	0.852
1.0	15	0.880
1.0	20	0.895

Nitric acid concentration

Only one acid, nitric acid, has so far been tried. With 0, 0.1, and 1 mg uranium, an increase in the acid concentration in a solution containing 20 ml of 3 molar NaN_3 is accompanied by increasing absorbancy at lower acidity and bleaching at higher acidity (Table II).

TABLE II

ABSORBANCY AS A FUNCTION OF ACID CONCENTRATION

Each solution contains 20 ml of 3 molar sodium azide per 25 ml of solution. γ = 360 mμ, slit width = 0.10 mm, 1 cm silica cells, reference water.

U *mg*	*Equivalent of 7 percent HNO_3 ml*	*Absorbancy*
0	0	0.033
0	5	0.032
0.1	1	0.093
0.1	5	0.111
0.1	15	0.122
0.1	30	0.112
0.1	60	0.047
1.0	1	0.835
1.0	5	0.895
1.0	15	0.915
1.0	30	0.895
1.0	60	0.046

Stability of the color

The yellow color produced when 1 mg U in 5 ml of 7 percent HNO_3 was treated with 20 ml of 3 molar sodium azide was stable for at least 20 hours.

Working curve

For the working curve (Fig. 2), a standard stock solution of uranium containing 1 mg uranium per ml in 7 percent nitric acid (7 + 93) was prepared from 99.9 percent U_3O_8 (MS-ST). Each solution measured contained the required amount of uranium, 5 ml of 7 percent HNO_3 (7 + 93) and 20 ml of 3 molar sodium azide all in a volume of 25 ml. The sodium azide was added last. Absorbancies were measured in 1-cm silica cells (corex will do), with a spectrophotometer, at a wavelength of 360 mμ and slit width of 0.10 mm corresponding to an effective band width of 0.7 mμ.

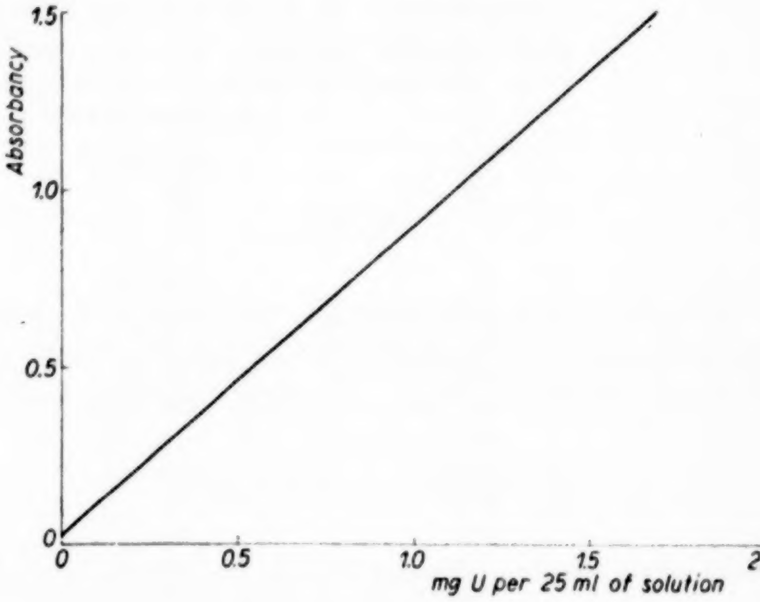

Fig. 2. Working curve.

Interfering elements

A systematic study of interfering elements has not as yet been made. However, under the conditions described, many hydroxides and azides would be expected to precipitate. Hence the application of the azide reaction to practical uranium analysis would require the absence of most of the other metals with the exception of the alkalis and the alkaline earths.

Procedure

Spectrophotometer with 1-cm silica or corex cells, can be used.

Nitric acid (7 percent). 70 ml of the concentrated acid are added to 930 ml of water.

Sodium azide (3 molar). 195 g of the best available sodium azide are dissolved in water at room temperature, filtered, and diluted to 1 liter in a volumetric flask.

The uranium-containing solution, free of interfering elements, preferably containing about 1 mg uranium in nitric acid solution, is evaporated to dryness in a beaker. The residue is dissolved in 5 ml of 7 percent nitric acid solution and transferred to a dry 25-ml volumetric flask. The beaker is rinsed with several small portions of the 3 molar sodium azide and transferred to the volumetric flask using only the sodium azide reagent for diluting to volume. Absorbancy is measured in the spectrophotometer at a wavelength of 360 mμ in a 1-cm cell using water as reference. Alternatively, a curve could be constructed using the reagents as reference and the procedure varied accordingly.

Hydrazoic acid and the metal azides are explosive and toxic and should be handled with care.

This investigation is part of a program being conducted by the Geological Survey on behalf of the Division of Raw Materials of the U.S. Atomic Energy Commission.

References p. 291

SUMMARY

A method has been devised for the spectrophotometric determination of uranium by means of the azide ion. The method possesses several advantages over the various thiocyanate procedures. It has a slightly higher sensitivity, an aqueous medium is used, and the reaction product is more stable. Within the concentration limits tested, BEER's law is obeyed.

RÉSUMÉ

Une méthode est proposée pour le dosage spectrophotométrique de l'uranium au moyen d'un azoture. Ce procédé présente plusieurs avantages sur les différentes méthodes au thiocyanate: sensibilité légèrement plus grande, emploi d'un milieu aqueux, produit de réaction plus stable. Dans les limites de concentrations essayées la loi de BEER est obéie.

ZUSAMMENFASSUNG

Eine Methode zur spektrophotometrischen Bestimmung von Uran mit Azid wird beschrieben. Diese Methode hat gegenüber den verschiedenen Thiocyanatverfahren mehrere Vorteile: etwas grössere Empfindlichkeit, wässriges Milieu, stabileres Reaktionsprodukt. Innerhalb der untersuchten Konzentrationsgrenzen ist das BEERS'sche Gesetz erfüllt.

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THE STANDARDIZATION OF ALUMINA FOR CHROMATOGRAPHIC SEPARATION OF POLYCYCLIC AROMATIC HYDROCARBONS

by

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INTRODUCTION

The use of activated alumina for chromatography has been well-established since the earliest days of the technique and various methods have been employed for standardizing its activity[1,2]. Earlier workers on separation of polycylic hydrocarbons[3,4,5,6,7,8] made no reference to standardization of alumina for their purpose. Indeed, as their object was in general preparative rather than analytical they had no need to define the activity of their column material. More recently the detection and determination of these compounds in various combustion products has become of great importance[9,10,11,12,13] especially as it is now possible to handle quantities of the order of a few micrograms and to determine one hydrocarbon in the presence of several others. A number of attempts have therefore been made to select alumina of suitable characteristics for the analysis of polycyclic aromatic hydrocarbons, but no reliable method has been found other than testing with hydrocarbons. Segregation according to particle size, and activity determination of each size range by the method of BROCKMANN AND SCHODDER[1] however, gives material which may vary greatly in its activity with reference to hydrocarbons. In earlier methods published from this laboratory it was the custom to select partially de-activated material. Thus COOPER[14] allowed a partly covered cannister of alumina to absorb moisture from the air until it was suitable for his purpose and COMMINS[15] added from 1.0 to 1.5 gram water to a freshly opened cannister and employed its contents when equilibrium had been established. Neither of these methods was wholly satisfactory as it could be standardized only for the life of the container of alumina.

Other workers[16] have prepared fully active alumina by keeping it permanently in a heated oven until required for use and employing mixed solvents such as benzene-cyclohexane mixtures for elution. This procedure is not suitable when analysing hydrocarbon mixtures with absorption peaks in the region of 220 to 280 mμ where benzene absorbs strongly.

METHOD

The present method is to adjust the activity of the alumina (Peter Spence, type H, 100/200 mesh) by exposing it to air over a solution of definite water vapour pressure in a desiccator. Sulphuric acid of known percentage by weight was used for this purpose. A useful method is to stack clock-glasses each covered with a thin layer of alumina and separated from its neighbour by a glass rod triangle, in an ordinary glass desiccator containing an ample supply of sulphuric acid of the correct composition. Alumina is taken for use after at least 48 hours directly from the equilibrator to prepare the columns.

The standardized method is based upon that of WEDGWOOD AND COOPER[11]. Columns are prepared in pyrex tubes of 1 cm diameter cut off obliquely at the lower end to facilitate the collection of fractions and the columns are formed upon a plug of glass wool previously extracted with cyclohexane. Even packing of the column is effected by stirring the alumina (about 5.5 g) with cyclohexane to form a thin slurry and pouring a little over the glass wool plug. A quantity of cyclohexane is then added to a depth of about 5 cm and the rest of the slurry poured through this column of solvent and the glass tube is tapped gently as the alumina settles. This method produces a column of more even packing than any other yet tried. The hydrocarbon solution, in volume of about 0.5 ml is added to the top of the column and collection of 3 ml fractions commenced. As soon as the solution has entered the column, additional quantities of cyclohexane are added, keeping a head of solvent suitable to the elution rate.

Using this technique a solution of mixed hydrocarbons was analysed. The solution contained 2 mg each of acenaphthylene, anthracene, fluoranthene and perylene in 100 ml of cyclohexane; thus the quantity of 0.5 ml placed on the column contained 10 μg of each hydrocarbon. These compounds were chosen because their chromatographic adsorbance extends over that of the range of hydrocarbons found in most combustion products. Successive eluates were examined in the S.P. 500 ultra-violet spectrophotometer and characteristic absorption peaks were sought at wavelengths of 340 (acenaphthylene), 376 (anthracene), 287.5 (fluoranthene) and 436 (perylene). The optical densities at each chosen wavelength were noted for every eluate. In all seven activities of alumina, prepared over 20, 50, 60, 65, 70, 75 and 80 per cent sulphuric acid were tested, and it was found that the best separation of the hydrocarbons amongst the fractions was achieved with alumina in equilibrium with 70 per cent sulphuric acid. For this alumina it was found that the four hydrocarbons separated in the above mentioned order at about the 4th, 10th, 16th and 50th fractions.

Although a complete separation is obtainable in these circumstances it should be noted that, for the accurate determination of a series of hydrocarbons, such a clear separation is not necessary provided that successive compounds in the elution sequence have measurable absorption peaks in their ultra-violet absorption spectra.

Further tests with cyclohexane extracts of the solids from air filtration plants have confirmed the usefulness of this method of standardizing the chromatographic separation of polycyclic aromatic hydrocarbons in microgram amounts. This method has also been applied to other combustion products such as cigarette smoke[17,18,19,20].

ACKNOWLEDGEMENT

The authors wish to acknowledge with thanks the support of the Department of Scientific and Industrial Research and of Imperial Chemical Industries, Ltd.

SUMMARY

Alumina for chromatographic separations of aromatic polycyclic hydrocarbons in micro-gram quantities is prepared by allowing it to come to equilibrium with water vapour from sulphuric acid of known concentration. The chromatographic procedure is described.

RÉSUMÉ

Une alumine est préparée en vue de séparations chromatographiques des hydrocarbures aromatiques polycycliques à l'échelle microchimique; on la met en équilibre avec la vapeur d'eau, à partir d'acide sulfurique de concentration connue. Le procédé chromatographique est décrit.

ZUSAMMENFASSUNG

Aluminiumoxyd wurde zur chromatographischen Trennung aromatischer polyzyklischer Kohlenwasserstoffe in Mengen von der Ordnung des Mikrogramms präpariert; hierzu wurde es mit dem Wasserdampf aus einer Schwefelsäure bekannter Konzentration ins Gleichgewicht gebracht. Das chromatographische Verfahren wird beschrieben.

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POLAROGRAPHY OF TITANIUM IN STRONG MINERAL ACID MEDIA

by

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The polarography of titanium has been reviewed by KOLTHOFF AND LINGANE[1]. It is well known that in mineral acid media of concentrations below about 0.1*M* the titanic-titanous couple does not behave reversibly. For example, a mixture of titanic and titanous chlorides in 0.01*M* hydrochloric acid shows a cathodic half-wave potential of —0.81 V *vs.* S.C.E. and an anodic half-wave potential of —0.14 V. If the couple behaved reversibly the cathodic and anodic half-wave potentials would be identical. Similar data are observed with dilute sulfuric acid as supporting electrolyte. On the other hand, the complexes present in citrate, tartrate, and oxalate media behave reversibly at the d.e. over certain pH ranges, and such media have been used almost exclusively for the practical polarographic determination of titanium.

The standard potential of the half-reaction

$$TiO^{+2} + 2\ H^+ + e = Ti^{+3} + H_2O \quad \dots\dots\dots\dots\dots\dots \quad (1)$$

is close to —0.15 V *vs.* S.C.E.[2]. The formal potential in 2 to 5*M* sulfuric acid agrees with this value when measured with a mercury (or other high hydrogen overvoltage) indicator electrode[3]. In 1*M* hydrochloric acid the formal potential is somewhat more reducing (—0.33 V *vs.* S.C.E.), reflecting chloride complexation of the quadrivalent titanium[3]. From the standard potential of reaction (1) the half-wave potential of the titanic-titanous couple with 0.01*M* hydrogen ion should be in the vicinity of —0.3 to —0.4 V *vs.* S.C.E. The observed cathodic half-wave potential is displaced from this value to a greater extent than the anodic half-wave potential. Thus, in dilute acid media the reduction of +4 titanium requires a larger overvoltage than does the oxidation of +3 titanium.

The reduction of the oxygenated TiO^{+2} must proceed by a more complex kinetic mechanism than does the oxidation of the aquo Ti^{+3} ion. It seemed likely that more nearly reversible behaviour would be observed with solutions containing a very high activity of hydrogen ion. This study has confirmed this prediction. With relatively concentrated solutions of hydrochloric, sulfuric, or phosphoric acids the reduction of +4 titanium and the oxidation of +3 titanium both approach reversibility. In addition to the beneficial effect of a very large hydrogen ion activity, complexation of the +4 titanium (and to a lesser degree +3 titanium) with chloride ion, hydrogen sulfate ion, and phosphoric acid is conducive to reversible behaviour. The characteristics of the polarographic waves in such strongly acid media are well suited to practical determinations of titanium, and these media (especially sulfuric and phosphoric acids) can be employed advantageously in analytical situations where the usual complexing media (citrate, tartrate, *etc.*) are inapplicable or undesirable. Sulfuric and phosphoric acid solutions are also advantageous in coulometric titrations with titanous ion generated electrolytically at a platinum cathode.

EXPERIMENTAL

Stock solutions of +4 titanium were prepared by adding water to pure $TiCl_4$. Chloride-free solutions in sulfuric acid were prepared by evaporating the aqueous titanyl chloride solution to fuming with concentrated sulfuric acid, followed by appropriate dilution. Chloride-free solutions in perchloric acid were obtained by adding a small excess of potassium permanganate to the titanyl chloride solutions, and removing the excess permanganate with just the requisite quantity of oxalic acid. All of these solutions were standardized in the usual way by reduction with zinc in a Jones reductor, and final titration with standard potassium dichromate solution after adding excess ferric ion.

Solutions of +3 titanium were prepared by reducing the titanyl solutions in a Jones reductor.

The usual polarographic technique with the dropping mercury electrode was employed, using an H-cell with a saturated calomel electrode as auxiliary electrode. In cases where chloride ion was to be excluded from the test solution the modified H-cell designed by CARRITT (Reference 1, p. 365) was used.

The polarograms were recorded automatically (at 25° C) but to economize on space tracings were prepared for reproduction herein.

Polarographic characteristics

Hydrochloric and perchloric acid media. The trend toward reversibility of the titanic-titanous couple with increasing concentration of hydrochloric acid is demonstrated by the typical polarograms in Fig. 1. These polarograms were obtained with solutions containing equal concentrations of +4 and +3 titanium. With concentrations of hydrochloric acid greater than about 1*M* the anodic wave is inaccessible to measurement, because it is masked by the anodic dissolution current of mercury; *i.e.*, at the higher hydrochloric acid concentrations +4 titanium is reduced by mercury.

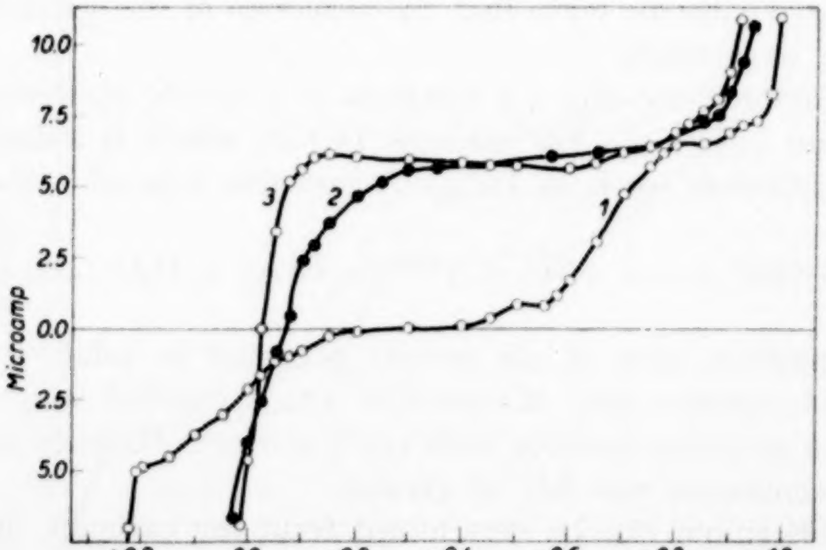

Fig. 1. Polarograms of equimolar mixtures (4.17 millimolar) of +4 and +3 titanium in (1) 0.2, (2) 4, and (3) 6*M* hydrochloric acid.

With 0.2M hydrochloric acid the couple is highly irreversible, as shown by the large separation of the cathodic and anodic waves. Since the formal potential is in the neighborhood of —0.2 to —0.3 V *vs.* S.C.E., it is evident that the reduction of the +4 titanium requires a larger overpotential than does the oxidation of the +3 titanium.

The marked positive shift of the reduction wave with increasing concentration of hydrochloric acid must mean that hydrogen and chloride ions are consumed in the cathodic reaction. That hydrogen and chloride ions both are required for reversible behaviour is demonstrated by the fact that irreversible type polarograms are observed in concentrated potassium chloride solutions containing less than about 1M hydrochloric acid. Furthermore, as shown by the polarograms of Fig. 2 in concentrated perchloric acid solutions, a high concentration of hydrogen ion alone does not produce reversible behaviour. In 8M perchloric acid (curve 2) the +3 titanium has been practically all oxidized by perchlorate ion, and it is evident from the attenuated cathodic wave that the reduction of the quadrivalent titanium (TiO^{+2}) is highly irreversible.

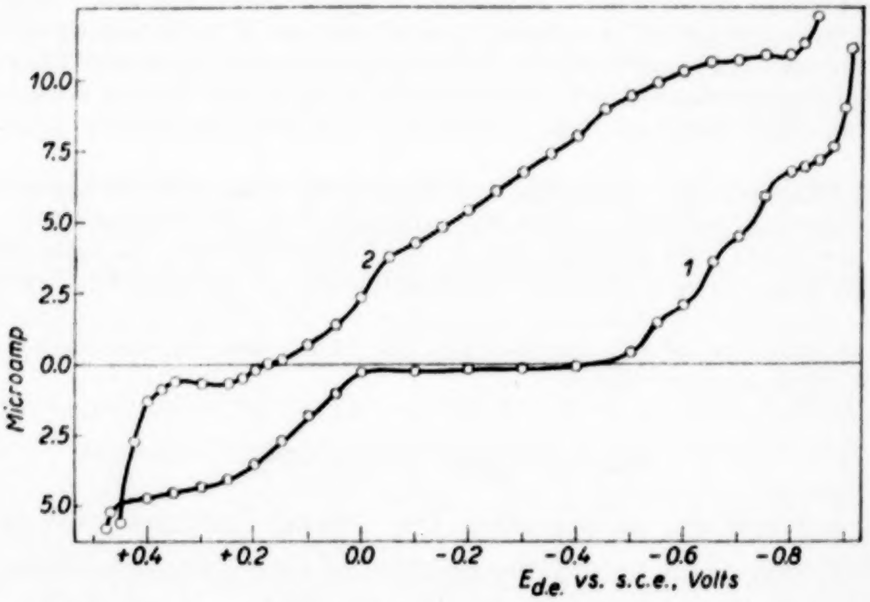

Fig. 2. Polarograms of equimolar mixtures (4.17 millimolar) of +4 and +3 titanium in (1) 1, and (2) 8M perchloric acid.

It is clear, therefore, that the +4 titanium in 3 to 6M hydrochloric acid must exist chiefly as an oxy-chloro ion, such as $TiOCl^+$, which is reduced to a chloro complex of +3 titanium, such as $TiCl_4^-$. A probable type of half-reaction is then

$$TiOCl^+ + e + 2\,H^+ + 3\,Cl^- = TiCl_4^- + H_2O \quad . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

The marked positive shift of the formal potential in relatively concentrated hydrochloric acid explains why MALMSTADT AND ROBERTS[4] were able to reduce +4 titanium at a platinum cathode with 100% current efficiency when the hydrochloric acid concentration was 6M or greater.

Although +4 titanium can be determined from the cathodic diffusion current in strong hydrochloric acid media, such media are not satisfactory for determining +3 titanium because measurement of the anodic diffusion current entails too large a correction for the anodic dissolution current of mercury.

Sulfuric acid media. The typical polarograms in Fig. 3 demonstrate that the titanic-titanous couple is very irreversible in 0.2*M* sulfuric acid, but becomes reversible with 4*M* or larger sulfuric acid concentrations. This conclusion is substantiated by all of the usual criteria for polarographic reversibility; *i.e.*, slope of log plots, equality of cathodic and anodic half-wave potentials, and absence of inflection at zero current with the composite anodic-cathodic waves.

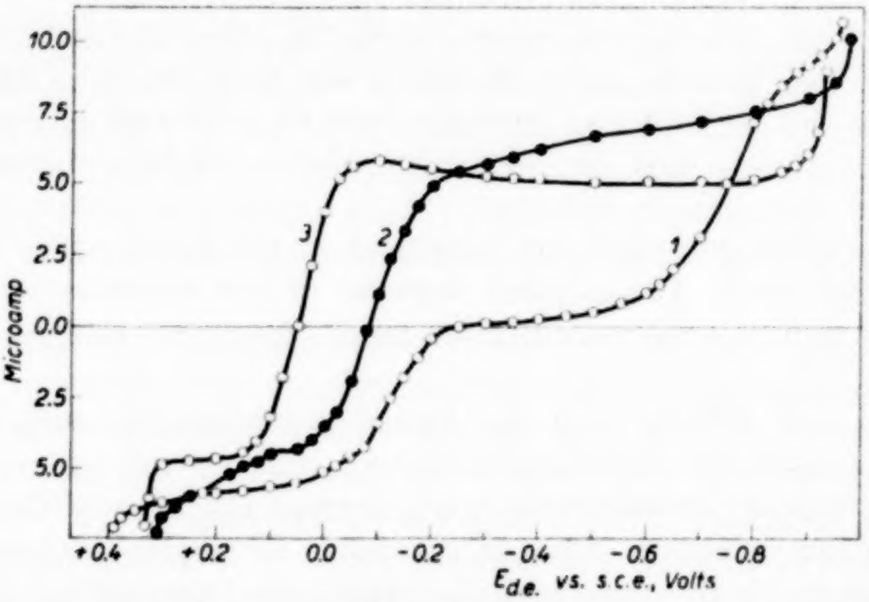

Fig. 3. Polarograms of equimolar mixtures (4.17 millimolar) of +4 and +3 titanium in (1) 0.2, (2) 4, and (3) 8*M* sulfuric acid.

Since the couple is irreversible in strong perchloric acid (Fig. 2) but reversible in fairly strong sulfuric acid, complexation of the +4 titanium in sulfuric acid is evident. Such complexation must involve hydrogen sulfate ion rather than sulfate ion, because the concentration of sulfate ion in moderately concentrated sulfuric acid solutions is very small. This conclusion is substantiated by the fact, demonstrated in Fig. 4, that addition of a large concentration of HSO_4^- alone (as $NaHSO_4$) to a

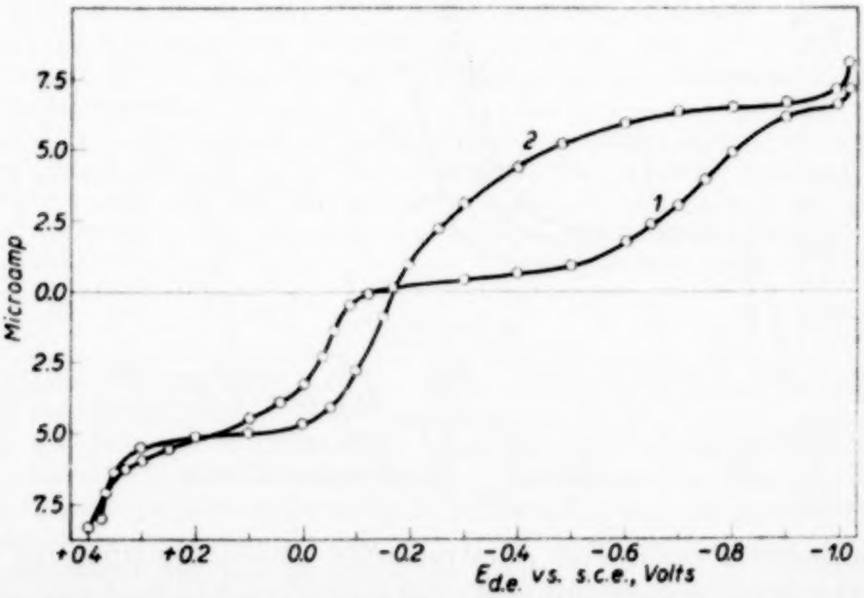

Fig. 4. Polarograms of equimolar mixtures (4.17 millimolar) of +4 and +3 titanium in sodium bisulfate and ammonium sulfate solutions. (1) 4*M* ammonium sulfate and 0.2*M* sulfuric acid; (2) 4*M* sodium bisulfate and 0.2*M* sulfuric acid.

dilute sulfuric acid solution produces a polarogram (curve 2) that approximates quite closely to the type characteristic of reversibility, but regardless of how large the sulfate ion concentration is (curve 1) the composite wave retains its highly irreversible characteristics.

The reversible half-wave potentials (virtually identical with the formal potentials) and diffusion current constants at 25° for the cathodic waves as functions of the sulfuric acid concentration are as follows.

(H_2SO_4), *M*	4	6	9	10	12	15
$E_{1/2}$ *vs.* S.C.E., V	−0.05	+0.033	+0.088	+0.098	+0.11	+0.17
$i_d/C\ m^{2/3}t^{1/6}$	0.93	0.97	0.64	0.61	0.41	0.36

The diffusion current constants are expressed in the usual units, microamp. per millimole per $mg^{2/3}sec^{-1/2}$. The marked decrease of the diffusion current constant with increasing sulfuric acid concentration results from the relatively large increase in viscosity.

Above about 4*M* sulfuric acid the formal potentials are sufficiently positive (oxidizing) to permit the electrogeneration of titanous ion by reduction of +4 titanium at a platinum cathode with 100% current efficiency without interference from hydrogen ion reduction. Thus, it is feasible to employ a platinum generator cathode for coulometric titrations with electrogenerated titanous ion in 4*M* or greater concentrations of sulfuric acid.

Phosphoric acid media. We were surprised to discover that the titanic-titanous couple behaves perfectly reversibly in even relatively dilute (1*M*) phosphoric acid. Fig. 5 exemplifies the excellent development of both the cathodic and anodic waves in 1 to 10*M* phosphoric acid. The polarographic characteristics are far superior to those in any of the other strong mineral acid media, and indeed are as good or better than in any of the supporting electrolytes heretofore used for the polarographic determination of titanium.

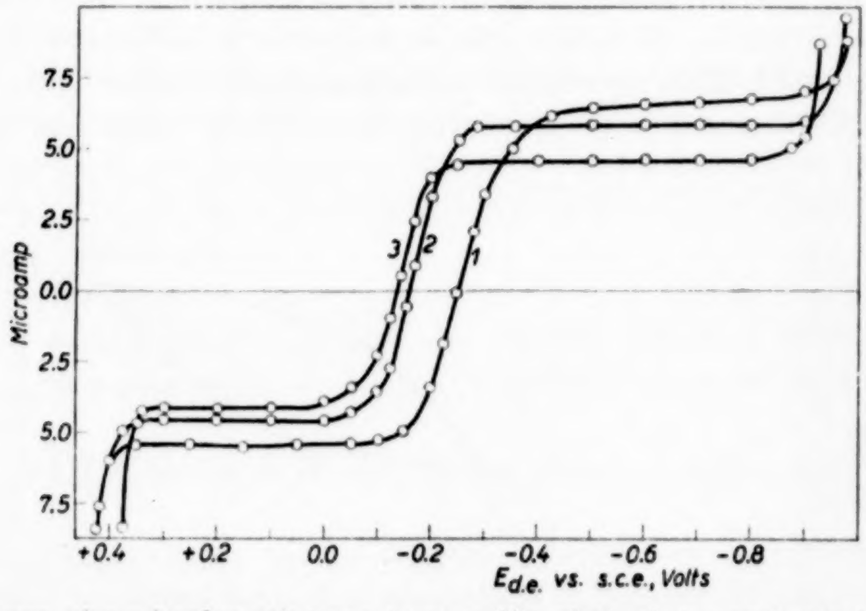

Fig. 5. Polarograms of equimolar mixtures (4.17 millimolar) of +4 and +3 titanium in (1) 1 (2) 5, and (3) 10*M* phosphoric acid.

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The half-wave potentials and diffusion current constants of +4 titanium in various concentrations of phosphoric acid at 25° are as follows:

(H_3PO_4), M	1	5	10	15
$E_{1/2}$ *vs.* S.C.E., V	—0.25	—0.15	—0.12	—0.09
$i_d/C\ m^{2/3}t^{1/6}$	1.39	1.23	0.780	0.341

The pronounced decrease in the diffusion current constant with increasing phosphoric acid concentration results from the decreased diffusion coefficient produced by the relatively great viscosity of the more concentrated solutions. The anodic half-wave potentials of +3 titanium are identical with the cathodic half-wave potentials of +4 titanium. Plots of E *vs.* log $i/(i_d\text{-}i)$ produced straight lines with a reciprocal slope of 0.061 V in excellent agreement with the 0.059 V for a reversible 1-electron reaction.

With 1M phosphoric acid hydrolytic precipitation of +4 titanium was observed after 24 hours, but with 4M or greater concentrations of phosphoric acid the solutions (up to 10 millimolar titanium) remain perfectly clear for at least a week. When the concentration of +4 titanium is much above 10 millimolar hydrolytic precipitation does occur quite rapidly even with the higher concentrations of phosphoric acid. This is no practical limitation because concentrations above 10 millimolar need not be used for polarographic determinations.

ACKNOWLEDGEMENT

Appreciation is expressed to the Mallinckrodt Chemical Works for partial financial support of this study, and to the National Science Foundation for a fellowship held by one of us (J.H.K.).

SUMMARY

The polarographic characteristics of the titanic-titanous couple have been investigated in moderately concentrated aqueous solutions of hydrochloric, perchloric, sulfuric, and phosphoric acids.

In 4 to 15M sulfuric acid the reversible formal potential becomes more positive (oxidizing) than the potential of hydrogen ion reduction on platinum, and sulfuric acid solutions can be employed advantageously for coulometric titrations with electrogenerated titanous ion using a platinum generator cathode.

Phosphoric acid (1 to 15M) is the best of these media for practical polarographic determinations of titanium. The couple behaves perfectly reversibly, the cathodic and anodic waves are both excellently developed, and the half-wave potential (—0.25 to —0.09 V *vs.* S.C.E.) is such that determination of titanium in the presence of several of the elements with which it is commonly associated is possible.

RÉSUMÉ

Les caractéristiques polarographiques du couple titane(III)/titane(IV) ont été examinées en solutions aqueuses moyennement concentrées des acides chlorhydrique, perchlorique, sulfurique et phosphorique.

Dans l'acide sulfurique 4 à 15M le potentiel réversible devient plus positif (oxydant) que le potentiel de réduction de l'ion hydrogène sur le platine. Les solutions d'acide sulfurique peuvent donc être utilisées avantageusement pour le titrage coulométrique au moyen de titane(III) formé par voie électrique sur une électrode de platine.

L'acide phosphorique (1 à 15M) est le milieu qui convient le mieux pour les dosages polarographiques du titane. La réaction est tout à fait réversible, les vagues cathodiques et anodiques obtenues sont excellentes et le potentiel de demi-vague (—0.25 à —0.09 V E.C.S.) est tel qu'il est possible de doser le titane en présence de plusieurs éléments l'accompagnant généralement.

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ZUSAMMENFASSUNG

Die charakteristischen polarographischen Eigenschaften des Paares Ti(III)/Ti(IV) wurden in mässig konzentrierten wässrigen Lösungen von Salzsäure, Perchlorsäure, Schwefelsäure und Phosphorsäure untersucht.

In 4 — 15*M* Schwefelsäure wird das reversibele Potential positiver (oxydierender) als das Potential der Wasserstoffionenreduktion an Platin. Schwefelsaure Lösungen können also für coulometrische Titrationen mit elektrisch an einer Platinkathode gebildetem Ti(III) verwendet werden.

Phosphorsäure (1 bis 15*M*) eignet sich am besten für praktische polarographische Titanbestimmungen. Die Reaktion ist vollkommen reversibel, die kathodischen und anodischen Wellen sind ausgezeichnet entwickelt und das Halbwertspotential (—0.25 bis —0.09 V gegenüber der gesättigten Kalomelektrode) ist so, dass das Titan in Gegenwart verschiedener Elemente mit denen es vergesellschaftet vorkommt, bestimmt werden kann.

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BUCHBESPRECHUNG

Rechentafeln zur chemischen Elementaranalyse von R. KRZIKALLA, Verlag Chemie, Weinheim, 1956, 232 Seiten, DM. 12.—.

Der Referent betrachtet es als einen gut gelungenen Versuch des Verfassers, dem organischen Chemiker ein brauchbares Tabellenwerk in die Hand zu geben, das ein sicheres und rasches Rechnen in der Elementaranalyse erlaubt. Die vorliegenden Tabellen ermöglichen es, die prozentuale Zusammensetzung einer chemischen Verbindung zu berechnen und darüber hinaus erlauben sie das Aufsuchen der Prozentzahlen unabhängig von der Elementarzusammensetzung. Weiterhin kann man mit Hilfe dieser Tabellen die Bruttoformel aus den gefundenen Prozentzahlen aufstellen.

Das Buch hat eine weite Anwendbarkeit, da man mit diesem Berechnungen für Verbindungen jeder denkbaren Zusammensetzung durchführen kann. Angenehm ist, dass dabei kleine Analysenfehler, soferne sie sich innerhalb der Fehlergrenzen befinden, nicht stören. Aus Zweckmässigkeitsgründen wurde der Umfang des Buches so gewählt, dass die Berechnung von Verbindungen bis zum Molekulargewicht 1000 als obere Grenze möglich ist. Es sind dabei diejenigen Verbindungen erfasst, die die folgenden Elemente und deren Vielfache enthalten:
C_1-C_{50}, H_1-H_{80}, O_1-O_{30}, N_1-N_{10}, S_1-S_8, P_1-P_4, $(CH_3O)_1$-$(CH_3O)_{10}$, F_1-F_{10}, Cl_1-Cl_{12}, Br_1-Br_4, J_1-J_4, Si_1-Si_8, B_1-B_2, As_1-As_2 und die Metalle bis $(Na, K)_4$, $(Li, Mg, Fe, Co, Ni, Cu, Ag)_3$, $(Ca, Al, Ti, V, Cr, Mn, Zn, Sn, Sb, Ba, Au, Hg, Pb, Bi, U)_2$, $(Zr, Mo, W)_1$.

Hervorzuheben ist, dass der in dem Buch enthaltene Text in den drei Sprachen: deutsch, englisch, französisch, erscheint, wodurch eine weite Verbreitung gesichert scheint. Mit diesem Buch ist ein wertvoller Beitrag zur Erleichterung der täglichen Analysenarbeit und Forschungsarbeit, soweit es die rechnerischen Belange betrifft, gegeben.

G. GORBACH (Graz)

TRANSFERT IONIQUE, ACIDES ET ACIDITÉ

par

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A. INTRODUCTION

Si à l'heure actuelle les propriétés physico-chimiques par lesquelles se manifestent les acides sont bien connues, l'explication de l'origine de ces propriétés est mal établie. Celle-ci est devenue d'autant plus difficile que les chimistes font de plus en plus appel à des solvants les plus divers. Des notions qui étaient nées de la chimie des solutions aqueuses doivent être généralisées de façon à leur donner un domaine d'application plus large. Aussi n'est-il point étonnant de constater qu'il y a au moins quatre théories des acides essayant chacune de trouver un caractère commun à tous les systèmes qui manifestent des propriétés acides. Ces quatre théories sont[1]:

a) la théorie du solvant
b) la théorie du proton
c) la théorie du cation-anion
d) la théorie électronique.

Cette dernière, due à LEWIS, est la plus générale; elle rattache la notion d'acide à un type de réaction très étendu. Elle peut s'appliquer aussi bien à des systèmes dissociés que non. Si l'on se limite à des systèmes dans lesquels les propriétés acides sont liées à des phénomènes d'ionisation et de dissociation, les trois premières théories citées recouvrent ensemble la plupart des données expérimentales connues.

GUTMANN ET LINDQVIST[2] ont récemment avancé une théorie qui permet de ramener ces trois théories à une seule: la théorie du transfert ionique.

Certaines idées que GURNEY[3] a formulées pour le cas particulier du transfert protonique peuvent être appliquées à la théorie de GUTMANN ET LINDQVIST. La définition d'une force d'acide par MANDEL[4] permet une comparaison aisée de différents acides dans divers solvants, même si le mécanisme de transfert est différent pour chacun d'eux.

Le but de ce travail est de montrer l'utilité de la théorie du transfert ionique pour la compréhension des phénomènes d'acidité. Il comprendra un rapide aperçu de la théorie tout à fait générale, une discussion détaillée du transfert protonique, pour lesquels les données sont les plus nombreuses et, finalement, l'utilité de la notion d'acidité sera discutée.

B. THÉORIE DU TRANSFERT IONIQUE

Le caractère acido-basique d'une molécule résulte de l'interaction entre solvant et molécule considérée et s'accompagne de la dissociation de celle-ci. Cette dissociation est le résultat du transfert d'un ion entre la molécule acido-basique et une molécule de solvant. L'ion transféré doit être simple et le solvant doit pouvoir le transférer lui-même d'une molécule à l'autre: il effectue alors un auto-transfert. Une molécule sera acide si elle transfère un cation sur une molécule de solvant et augmente ainsi la concentration en particules les plus positives du solvant. Une base transfère un anion sur le solvant et augmente la concentration en particules les plus négatives. La réciproque de cette définition est valable: ainsi, si le solvant transfère un anion sur une molécule de soluté, celle-ci présentera des propriétés acides.

Soit le solvant s-p (où p est un atome pouvant donner un ion positif). On aura alors:

Réaction d'auto-transfert $2\ \mathrm{sp} \rightleftarrows \mathrm{sp_2}^+ + \mathrm{s}^-$
Réaction acide $\mathrm{Ap} + \mathrm{sp} \rightleftarrows \mathrm{sp_2}^+ + \mathrm{A}^-$
Réaction basique $\mathrm{B} + \mathrm{sp} \rightleftarrows \mathrm{Bp}^+ + \mathrm{s}^-$

Soit le solvant S-n (où n peut donner un anion). Dans ce cas:

Réaction d'autotransfert $2\ \mathrm{Sn} \rightleftarrows \mathrm{S}^+ + \mathrm{Sn_2}^-$
Réaction acide $\mathrm{A} + \mathrm{Sn} \rightleftarrows \mathrm{S}^+ + \mathrm{An}^-$
Réaction basique $\mathrm{Bn} + \mathrm{Sn} \rightleftarrows \mathrm{B}^+ + \mathrm{Sn_2}^-$

Les cas du premier exemple peuvent être illustrés dans l'eau par l'acide chlorhydrique et l'ammoniaque. Pour le deuxième on peut choisir le chlorure arsénieux ($2\ \mathrm{AsCl_3} \rightleftarrows \mathrm{AsCl_2}^+ + \mathrm{AsCl_4}^-$) comme solvant; comme acide le chlorure ferrique et comme base le chlorure de tétra-méthylamine[5].

Dans le cas de l'eau cette conception de l'acide recouvre celle de BRÖNSTED avec cette différence que dans la dernière la réaction fondamentale est la dissociation de la molécule d'acide ou du solvant avec libération d'un proton, tandis qu'ici c'est le mécanisme plus ou moins complexe du transfert proprement dit qui est fondamental. Des preuves directes de la théorie n'existent pas encore mais un série de justifications peuvent être fournies: l'existence de $\mathrm{H_3O^+}$ et la très courte durée de vie moyenne de cette particule, indiquent un transfert continuel du proton de molécule d'eau en molécule d'eau („random transfer")[6]; d'autre part, on peut se baser sur la grande mobilité électrique des protons dans des solvants pouvant échanger des protons, la conductivité élevée de $\mathrm{SO_2}$ dans $\mathrm{SO_3}$ liquide[7] pouvant s'expliquer par un transfert de l'ion $\mathrm{O^{-2}}$ (montrée par réactions d'échange isotopique[2,8]). Une discussion détaillée pour le cas particulier de l'$\mathrm{AsCl_3}$ est donnée par LINDQVIST[5].

Il manque actuellement des données expérimentales détaillées en ce qui concerne les solvants réalisant des transferts non-protoniques. D'autre part, il semble que le proton soit le seul cation participant aux transferts ioniques[2]. Nous nous limiterons dans la suite uniquement à la discussion des transferts protoniques, étant entendue que *toutes les conclusions restent valables pour les transferts anioniques à condition de remplacer la notion d'acide par celle de base.*

C. TRANSFERTS PROTONIQUES

Suivant GURNEY[3], le transfert protonique peut être caractérisé par une énergie de transfert J, définie de la façon suivante

$$J = \frac{\Delta G'}{N} = -kTlgK \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

où $\Delta G'$ est l'énergie libre de Gibbs propre[9], N le nombre d'Avogadro, k la constante de Boltzmann, T la température absolute et K la constante d'équilibre de la réaction de transfert. Nous pouvons schématiser celle-ci de la façon suivante

$$AH + sH \rightleftharpoons A^- + sH_2^+. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

AH est l'acide et sH le solvant. La constante d'équilibre de la réaction de transfert est reliée à la constante d'acidité de Brönsted par la rélation suivante

$$K = \frac{Ka}{M} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

où M est l'activité du solvant sH, égale à sa molalité dans le cas des solutions pas trop concentrées en acide.

L'énergie de transfert protonique J apparaît comme le travail qu'il faut fournir pour transférer un proton de la molécule acide AH sur celle du solvant (cette énergie est souvent exprimée en électrons-volt). Il en résulte que l'on peut définir une probabilité de transfert qui sera proportionnelle à exp. $(-J/kT)$. Plus J sera grande, plus cette probabilité sera faible. Si J tend vers zéro, la probabilité tend vers une certitude et l'acide AH tend à devenir fort.

Suivant Gurney, nous distinguons deux parties dans cette énergie de transfert de proton:

$$J = J_1 + J_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

L'énergie de transfert intrinsèque, J_1, est la différence entre les affinités pour le proton de l'ion ou la molécule A et le solvant sH. C'est encore la différence entre les niveaux énergétiques quantiques de toutes les particules présentes avant et après le transfert. Comme pour les molécules ordinaires les plus simples les niveaux quantiques de vibration sont très écartés, dans tout le domaine de température facilement accessible aux expériences acido-basiques, cette energie sera constante et on peut considérer J_1 comme indépendante de la température.

L'énergie interactionnelle J_2 résulte de l'interaction électrostatique de toutes les charges présentes après le transfert de proton et de l'interaction de ces charges avec le solvant, de quelque nature qu'elle soit. Comme on verra dans la suite, ces deux phénomènes doivent dépendre de la température; il en sera de même pour J_2.

Cette séparation de l'énergie de transfert protonique en deux parties nettement différentes, corrobore celle des acides en ionogéniques et isoioniques[10]. Les premiers correspondent à des réactions de transfert dans lesquelles il y a augmentation du nombre total de particules chargées tandis que pour les seconds, ce nombre reste constant. Ces derniers se caractérisent par une énergie interactionnelle J_2 particulièrement faible étant donné que du point de vue de l'interaction, la situation globale est peu changée par le transfert de proton. Expérimentalement, cette distinction se manifeste par la façon différente dont varie la constante Ka en fonction de la température.

Il est difficile, à l'heure actuelle, de préciser avec plus de détails l'énergie de transfert protonique et de la rattacher aux autres propriétés physico-chimiques des molécules d'acide et de solvant.

En ce qui concerne l'énergie intrinsèque, les données de la chimie théorique ne permettent pas encore de calculer les valeurs de J_1 à priori pour un couple solvant-acide. Tout au plus est il possible d'établir une relation entre l'énergie J_1 d'une molécule dans un solvant (par exemple l'eau) et celle de ce même acide dans un autre solvant (soit sH). On doit, en effet, avoir*

$$(J_1)^{\mathrm{sH}}_{\mathrm{AH}} = (J_1)^{\mathrm{H_2O}}_{\mathrm{AH}} - (J_1)^{\mathrm{H_2O}}_{\mathrm{sH}} + (J_1)^{\mathrm{sH}}_{\mathrm{sH}} \quad \ldots\ldots\ldots\ldots \quad (5)$$

Il faut donc connaître l'énergie de transfert protonique intrinsèque de la molécule sH dans l'eau et l'énergie intrinsèque d'autotransfert du solvant sH. L'énergie d'autotransfert d'un solvant sH est déterminée de la façon suivante

$$(J)^{\mathrm{sH}}_{\mathrm{sH}} = -\,kTlgK_{\mathrm{sH}} = -\,kTlgk_{\mathrm{sH}} + 2\,kTlgM \quad \ldots\ldots\ldots \quad (6)$$

si: $$k_{\mathrm{sH}} = [\mathrm{sH_2^+}]\,[\mathrm{s^-}] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

Une deuxième relation importante découle de (5). En effet on doit avoir

$$(J_1)^{\mathrm{sH}}_{\mathrm{AH}} - (J_1)^{\mathrm{sH}}_{\mathrm{BH}} = (J_1)^{\mathrm{s'H}}_{\mathrm{AH}} - (J_1)^{\mathrm{s'H}}_{\mathrm{BH}} \quad \ldots\ldots\ldots\ldots\ldots \quad (8)$$

Elle établit que la différence entre l'énergie de transfert intrinsèque de deux acides est indépendante de la nature du solvant. Si l'on connait les valeurs de J_1 d'une série d'acides dans un solvant et la valeur d'un entre eux dans un deuxième solvant, on trouve toutes les autres valeurs dans ce solvant.

Il ne semble pas possible d'établir des relations analogues pour l'énergie interactionnelle. GURNEY, en se basant sur une ancienne théorie essentiellement électrostatique de WYNNE-JONES[11], a suggéré la forme suivante pour J_2

$$J_2 = \frac{C}{\varepsilon} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

où ε est la constante diélectrique du solvant considéré et C une constante indépendante de la température et du solvant mais variant selon la nature de la molécule d'acide. Cette hypothèse permettrait de calculer J_2 à partir de la variation de J en fonction de la température, pour autant que l'on connaisse la constante diélectrique du solvant. Si cette hypothèse était exacte, on devrait trouver pour deux acides AH et BH la relation suivante

$$\log \frac{(Ka)_{\mathrm{AH}}}{(Ka)_{\mathrm{BH}}} = \frac{1}{kT}\,[(J_1)_{\mathrm{BH}} - (J_1)_{\mathrm{AH}}] + \frac{1}{kT}\,[C_{\mathrm{BH}} - C_{\mathrm{AH}}]\,\frac{1}{\varepsilon} \quad \ldots \quad (10)$$

---

* Nous utilisons la convention suivante: l'indice inférieur indique la nature de l'acide, l'indice supérieur le solvant.

Faisant usage de (8), on peut montrer que (10) doit avoir la forme prévue par la théorie de WYNNE-JONES

$$\log \frac{(Ka)_{\mathrm{AH}}}{(Ka)_{\mathrm{BH}}} = A + \frac{B}{\varepsilon} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

où A et B sont deux constantes qui ne dépendent que des acides AH et BH. Or on sait, et le graphique de la Fig. 1 le montre, que cette relation n'est vérifiée que pour certains couples d'acides et pas pour d'autres. (Les valeurs numériques pour les *pKa* ont été empruntées au travail d'IZMAÏLOV[12].)

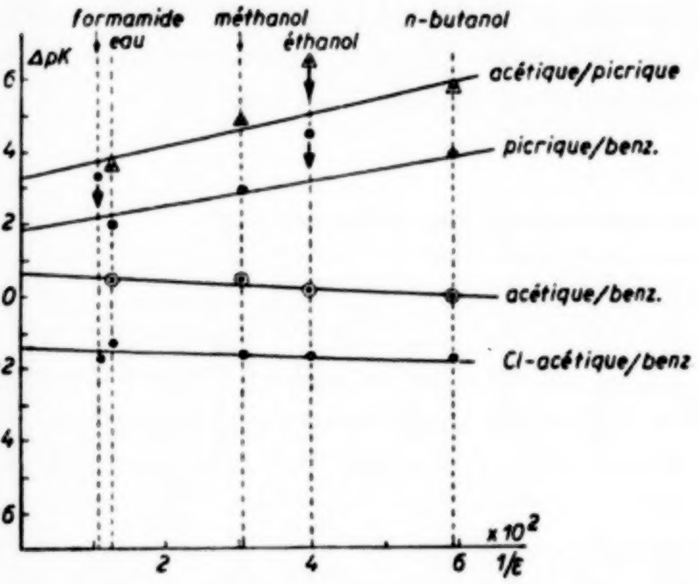

Fig. 1. ΔpK pour différents couples d'acides en fonction de $^1/\varepsilon$.

Le mécanisme du transfert de proton permet de comprendre pourquoi cette hypothèse n'est que partiellement vérifiée. On admet actuellement que la dissociation d'un acide débute par la formation d'un complexe selon une réaction du type

$$\mathrm{AH} \ldots \mathrm{sH} \rightleftharpoons \mathrm{A^-} \ldots \mathrm{H^+sH} \qquad (12)$$

où la ligne pointillée indiquerait éventuellement une liaison d'hydrogène. Une fois le transfert réalisé à l'intérieur de complexe AH ... sH, on a l'analogue d'une molécule avec une liaison à caractère électrostatique qu'il faut dissocier. La dissociation doit s'opérer contre les forces électrostatiques et les forces à courte portée et sera caractérisée par J_2. Dans un milieu homogène et continu on aurait en première approximation une relation du type (9). Mais dans un solvant réel, ceci n'est plus exact, car au fur et à mesure que les charges se séparent les molécules dipolaires du solvant subissent l'action de celles-ci et les molécules qui sont situées à leur proximité s'orientent d'une façon bien caractéristique pour former des cosphères[3]. (Une cosphère est définie comme une sphère formelle ayant une charge au centre et un rayon tel qu'à l'extérieur de celle-ci les molécules du solvant ne subissent plus l'influence orientante de la charge centrale.)

La variation du potentiel au cours de la séparation des charges est représentée dans la Fig. 2[13]. Le complexe A⁻ ... H⁺sH est en équilibre en A. On sépare d'abord les charges le long de la courbe I, purement hypothétique puisque la constante diélectrique déterminant les forces électrostatiques varie tout au long de la séparation par suite de la ,,solvatation'' progressive des ions. Une fois les cosphères formées, celles-ci jouent le rôle de particules individuelles et forment le complexe en B. Ce complexe, plus ou moins stable entre ions solvatés, correspond à une paire d'ions associés dans le sens de BJERRUM[14]. Les cosphères peuvent être séparées le long de la courbe II dans un milieu de constante diélectrique bien définie où la contribution électrostatique sera maintenant C/ε, soit pratiquement la différence d'énergie potentielle entre B et

C, point où les ions solvatés se trouvent définitivement séparés. Il s'en suit que l'énergie interactionnelle totale J_2* aura la forme

$$J_2 = \frac{C}{\varepsilon} + \Delta J_2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$

où ΔJ_2 est la différence entre l'énergie potentielle des points A et B et tient compte essentiellement du phénomène de solvatation. ΔJ_2 peut être positive, négative ou zéro mais son évaluation reste difficile car elle nécessite la connaissance exacte de la structure de la solution. Tout ce que l'on peut prédire, c'est que probablement toute la contribution entropique à l'énergie de transfert sera contenue dans ΔJ_2. Mais des considérations macroscopiques seules ne suffisent pas à préciser la valeur de ΔJ_2. L'étude de la force d'acidité dans différents solvants permettra d'apporter une certaine contribution à la connaissance de ce facteur inconnu.

TABLEAU I

pKa DE DIVERS ACIDES DANS DIFFÉRENTS SOLVANTS (25° C)[12]

Constante diélectrique	*90*	*78.5*	*31.5*	*25*	*17*	*12.5*	*6.1*	*24*	*15*
Acides	*Formamide*	*Eau*	*Méthanol*	*Éthanol*	*n-Butanol*	*Pyridine*	*Acide acétique*	*90% Acétone*	*73.5% Dioxane*
Ac. acétique	—	4.75	9.7	10.4	10.35	—	—	10.27	8.75
,, mono-Cl-acétique	4.56	2.86	7.8	8.5	8.5	—	—	7.6	—
,, di-Cl-acétique	2.85	1.3	6.3	7.1	7.3	—	—	—	—
,, tri-Cl-acétique	1.46	0.7	4.9	5.7	6.3	—	11.46	—	—
,, benzoïque	6.23	4.2	9.4	10.1	10.2	9.8	—	9.8	8.6
,, *o*-NO$_2$-benzoïque	4.28	2.17	7.6	8.4	8.5	—	—	—	7.02
,, *o*-OH -benzoïque	4.42	2.98	7.9	8.6	8.73	—	—	7.22	6.82
,, *p*-OH -benzoïque	—	4.54	10.5	10.8	—	—	—	8.07	10.0
,, *p*-NO$_2$-benzoïque	—	3.42	8.4	8.9	9.1	—	—	8.09	7.32
Phénol	—	9.89	14.0	—	—	—	—	—	—
p-NO$_2$-phénol	8.5	7.16	—	11.0	12.65	—	—	10.93	—
2.4-Dinitrophénol	4.52	4.02	7.85	8.2	8.36	—	—	6.45	—
Ac. picrique	1.2	0.8	4.8	3.9	4.5	—	—	2.18	—
Ion anilinium	4.1	4.62	6.0	5.7	3.75	—	—	3.27	—
p-$CH_3C_6H_4NH_3^+$	—	5.12	6.6	6.2	—	—	—	4.15	—
Ion pyridinium	4.48	5.21	5.55	4.3	—	—	—	—	—
$C_2H_5NH_3^+$	—	10.75	—	12.0	11.49	—	—	—	—
Ac. nitrique	—	0.2	3.17	3.6	—	4.3	9.38	—	—
,, chlorhydrique	—	0.8	1.05	2.0	—	5.4	9.16	2.47	—

D. LA FORCE D'ACIDITÉ

La force d'acidité d'un acide dans un solvant donné peut être déterminée à l'aide de la constante d'acidité Ka. Mais la comparaison d'acides dans différents solvants ne peut plus se baser sur des considérations aussi simples, comme il résulte du Tableau I où les *pKa* de différents acides dans différents solvants ont été réunis.

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* En fait, J_2 contient aussi une contribution énergétique pour la formation du complexe initial qui sera très faible lorsque AH est une particule neutre et qui comprendra un terme de „solvatation'' plus important dans le cas d'un acide chargé. C'est ce qui permet de comprendre la différence entre acide isoionique et ionogénique.

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La définition de l'acidité par un transfert ionique en général et protonique en particulier, permet de définir une force d'acidité qui a un sens physique bien défini. Une molécule sera d'autant plus acide que la probabilité de transférer son proton sur une molécule de solvant sera élevée, soit J faible; il faut en plus que cette probabilité de transfert soit grande par rapport à la probabilité d'autotransfert du solvant.

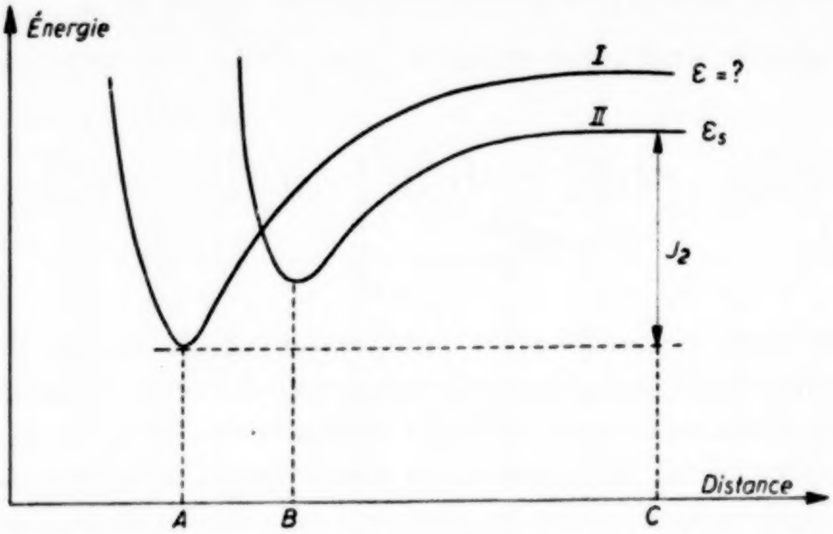

Fig. 2. Énergie potentielle d'interaction de deux ions pendant la dissociation acide.

Définissons une fonction X de telle façon que

$X = 0$, quand $(J)^{\mathrm{sH}}_{\mathrm{AH}} = (J)^{\mathrm{sH}}_{\mathrm{sH}}$; en effet, quand $(J)^{\mathrm{sH}}_{\mathrm{AH}} \geqslant (J)^{\mathrm{sH}}_{\mathrm{sH}}$, les propriétés acides ont disparu;

$X = 1$, quand $J = 0$; à partir de ce moment l'acide est fort et tout à fait dissocié. En outre, X sera, pour des acides non forts, compris entre 1 et 0 et d'autant plus près de 1 que l'acide est moins faible. La fonction suivante satisfait à ces critères:

$$X = 1 - \frac{(J)^{\mathrm{sH}}_{\mathrm{AH}}}{(J)^{\mathrm{sH}}_{\mathrm{sH}}} \quad \ldots\ldots\ldots\ldots\ldots \quad (14)$$

Deux acides comparés dans deux solvants différents seront de la même force si leur X sont identiques; à ce moment le rapport entre le logarithme de la probabilité du transfert protonique et le logarithme de la probabilité d'autotransfert du solvant sera le même. La Fig. 3 reproduit graphiquement la valeur de X pour quelques acides dans différents solvants.

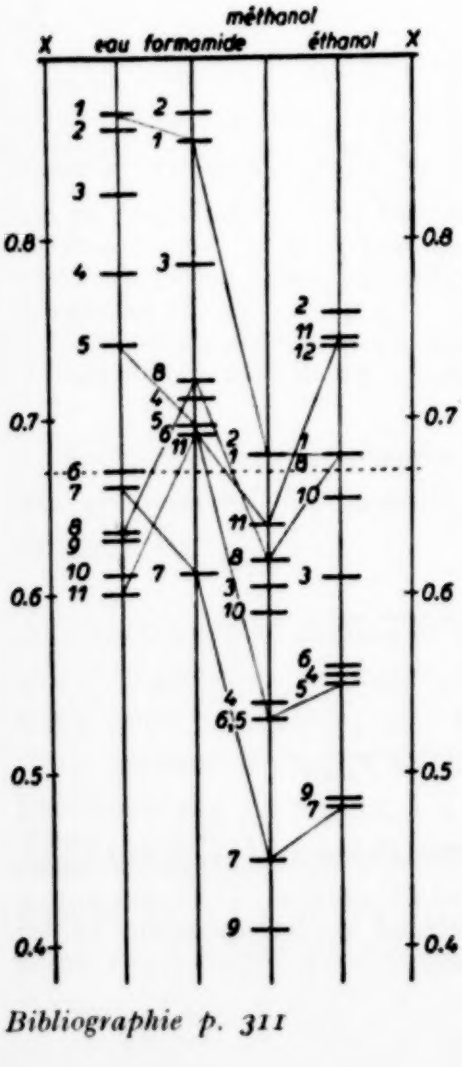

Fig. 3. Échelle des forces d'acidité dans différents solvants. 1. ac. tri-Cl-acétique. 2. ac. picrique. 3. ac. di-Cl-acétique. 4. ac. *o*-NO_2-benzoïque. 5. ac. Cl-acétique 6. 2,4-dinitrophénol. 7. ac. benzoïque. 8. ion anilinium. 9. ac. acétique. 10. ion *p*-CH_3-C_6H_4-NH_3. 11. ion pyridinium.

Il apparaît dans cette Fig. 3 que la variation de X d'un solvant à l'autre pour un acide est difficile à prévoir et à interpréter à première vue. Toutefois, la fonction de la force d'acidité permet de réaliser un certain nombre de faits importants. Introduisons la relation (5) dans (14) afin de comparer la valeur de X^{sH}_{AH} à celle de $X^{H_2O}_{AH}$ (une relation analogue peut être obtenue pour deux solvants quelconques). On obtient

$$X^{sH}_{AH} = \left[\frac{(J)^{sH}_{sH} - (J)^{sH}_{H_2O}}{(J)^{sH}_{sH}} - \frac{(J_1)^{sH}_{sH} - (J_1)^{H_2O}_{sH}}{(J)^{sH}_{sH}}\right] + \frac{(J_2)^{H_2O}_{AH} - (J_2)^{sH}_{AH}}{(J)^{sH}_{sH}} + \frac{(J)^{H_2O}_{H_2O}}{(J)^{sH}_{sH}} X^{H_2O}_{AH} \qquad (15)$$

Le premier terme entre parenthèse est indépendant de la nature de l'acide AH et déterminé uniquement par les propriétés des deux solvants. Le deuxième terme est proportionnel à la différence entre l'énergie interactionnelle de la molécule AH dans H_2O et sH. Le dernier terme, finalement, est une fonction linéaire de la force d'acidité dans le solvant H_2O, le coefficient de proportionnalité ne dépendant que des propriétés des deux solvants.

Les figures 4, 5 et 6 représentent des graphiques où la force d'acidité d'une série d'acides dans trois solvants différents a été tracée en fonction de la force d'acidité dans l'eau. L'examen de ces graphiques révèle les deux faits suivants:

a) Les acides se classent, en première approximation, selon un certain nombre de droites toutes parallèles, de pente $(J)^{H_2O}_{H_2O}/(J)^{sH}_{sH}$. L'existence de ces droites indique

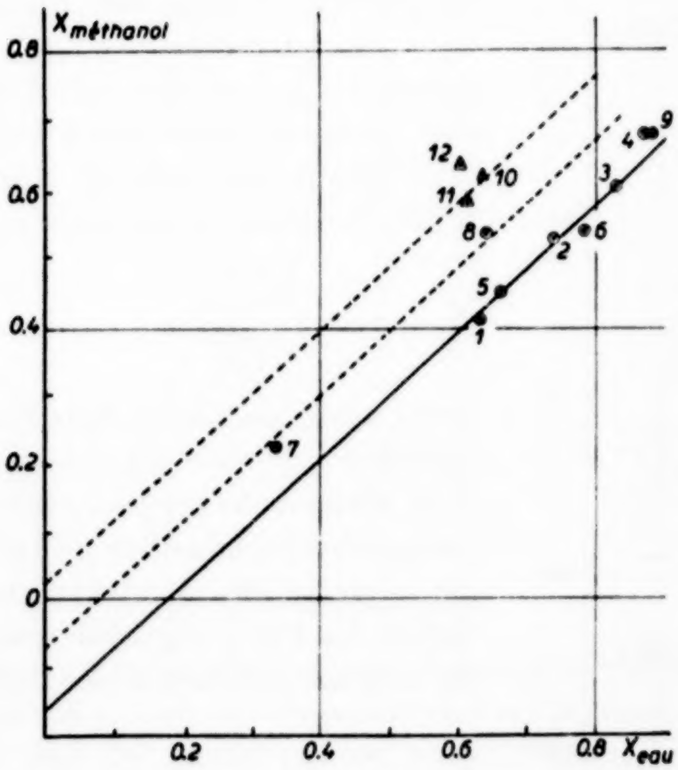

Fig. 4. Comparaison de la fonction X dans l'eau et le méthanol. Pente $= (J)^{H_2O}_{H_2O} / (J)^{méth.}_{méth.}$
1. ac. acétique. 2. ac. Cl-acétique. 3. ac. di-Cl-acétique. 4. ac. tri-Cl-acétique. 5. ac. benzoïque. 6. ac. o-NO_2-benzoïque. 7. phénol. 8. 2,4-dinitrophénol. 9. ac. picrique. 10. ion anilinium. 11. ion p-CH_3-anilinium. 12. ion pyridinium.

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qu'il existe des familles d'acides dont la variation de J_2 est la même quand on passe d'un solvant à un autre. Il est aisé, dans ces conditions, d'admettre que pour une telle famille l'énergie interactionnelle est la même dans un solvant donné. Les graphiques montrent que les trois droites correspondent

i) aux acides carboxyliques
ii) aux phénols
iii) aux amines et dérivés.

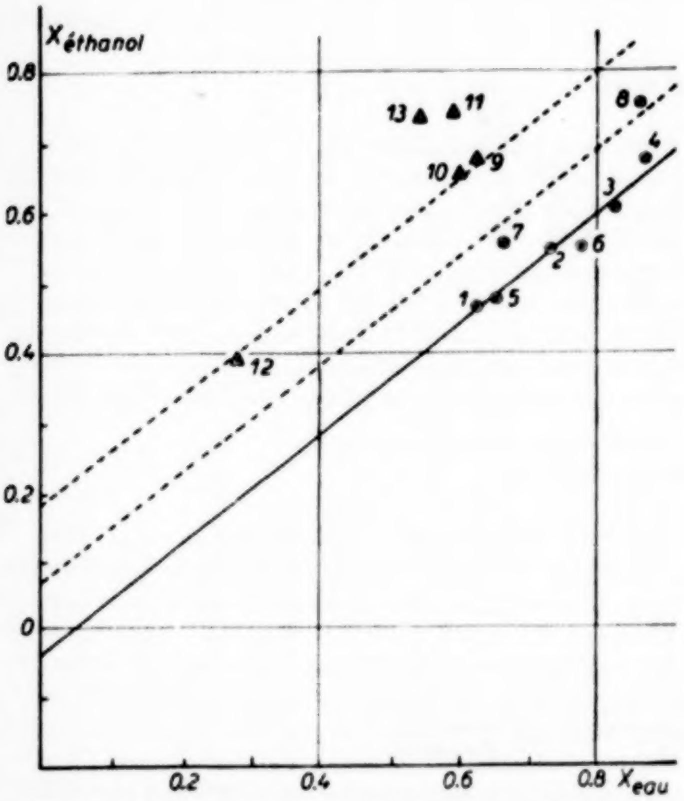

Fig. 5. Comparaison de la fonction X dans l'eau et l'éthanol. Pente = $\left(J\right)^{H_2O}_{H_2O} / \left(J\right)^{\text{éth.}}_{\text{éth.}}$
1. ac. acétique. 2. ac. Cl-acétique. 3. ac. di-Cl-acétique. 4. ac. tri-Cl-acétique. 5. ac. benzoïque. 6. ac. o-NO_2-benzoïque. 7. 2,4-dinitrophénol. 8. ac. picrique. 9. ion anilinium. 10. ion p-CH_3-anilinium. 11. ion pyridinium. 12. ion éthyl-aminium. 13. ion ethylanilinium.

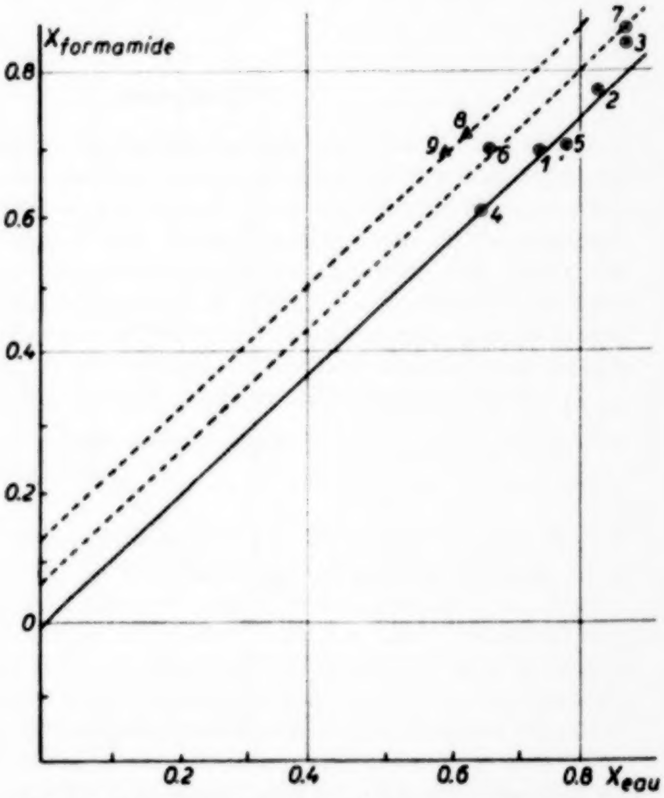

Fig. 6. Comparaison de la fonction X dans l'eau et la formamide. Pente = $\left(J\right)^{H_2O}_{H_2O} / \left(J\right)^{\text{form.}}_{\text{form.}}$
1. ac. Cl-acétique. 2. ac. di-Cl-acétique. 3. ac. tri-Cl-acétique. 4. ac. benzoïque. 5. ac. o-NO_2-benzoïque. 6. 2,4-dinitrophénol. 7. ac. picrique. 8. ion anilinium. 9. ion pyridinium.

Cette énergie interactionnelle J_2 serait donc essentiellement déterminée par la solvatation du groupement fonctionnel, les chaînes latérales à ces groupements influençant surtout sur J_1.

b) Les valeurs à l'origine de ces droites vont en croissant dans l'ordre acides carboxyliques — phénols — amines. Or, cette dernière famille correspond aux acides isoioniques pour lesquels J_2 doit être faible; il en sera de même pour la variation de J_2 d'un solvant à l'autre. Pour la droite correspondant aux amines, on peut égaler pratiquement la valeur à l'origine au terme constant de la relation (15). Pour les deux autres familles, le terme $(J_2)^{H_2O}_{AH} - (J_2)^{sH}_{sH}$ sera négatif; pour autant que les deux valeurs de J_2 soient positives, et cela resterait à démontrer, l'énergie interactionnelle dans l'eau serait plus faible que dans les trois autres solvants. Ceci permettrait d'expliquer le rôle privilégié que joue l'eau du point de vue de la dissociation électrolytique.

Dans la Fig. 7, les valeurs de X sont comparées dans le méthanol et dans la formamide, deux solvants pour lesquels les énergies d'autotransfert sont pratiquement identiques. Il apparaît que la différence entre les trois groupes d'acides est fortement atténuée. Même les acides isoioniques ne se distinguent à peine des autres. Ceci indiquerait une forte analogie dans les interactions entre acides et solvant, quelque soit la nature de l'acide.

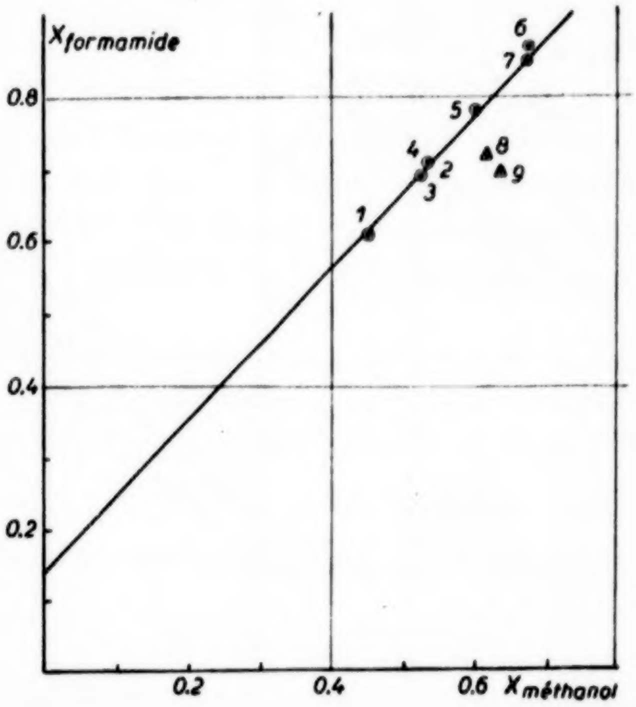

Fig. 7. Comparaison de la fonction X dans le méthanol et le formamide. Pente $= \left(J\right)^{\text{méth.}}_{\text{méth.}} / \left(J\right)^{\text{form.}}_{\text{form.}}$
1. ac. benzoïque. 2. ac. Cl-acétique. 3. 2,4-dinitrophénol. 4. ac. *o*-NO_2-benzoïque. 5. ac. di-Cl-acétique. 6. ac. picrique. 7. ac. tri-Cl-acétique. 8. ion anilinium. 9. ion pyridinium.

E. CONCLUSION

Le principe du transfert protonique, et de là du transfert ionique en général, fournit une théorie des acides intéressante. Il permet la définition d'une énergie de transfert qui peut être rattaché formellement aux propriétés physicochimiques des acides et solvants. Cette énergie de transfert rend possible également la comparaison de différents acides dans différents solvants, grâce à la fonction de force d'acidité qui a un sens physique bien défini. On peut espérer que l'étude expérimentale de J et X dans différents solvants et à différentes températures permette de trouver encore plus de renseignements sur le mécanisme du transfert ionique et sur l'interaction des molécules d'acides et de solvant.

REMERCIEMENTS

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RÉSUMÉ

Le transfert ionique en général et le transfert protonique en particulier sont présentés et discutés en vue d'une théorie de l'acidité et l'importance de l'énergie de transfert est montrée. Dans l'analyse de cette énergie, qui contient une partie intrinsèque et une partie interactionnelle, l'attention est attirée sur le fait que cette dernière ne peut pas, en général, être une fonction simple de la constante diélectrique du solvant. Par contre, la comparaison de la partie intrinsèque dans différents solvants est aisée. On peut définir, à partir de l'énergie de transfert, une fonction universelle de force d'acidité X qui a un sens physique très précis. Par la comparaison de cette fonction X dans plusieurs solvants, il apparaît que la partie interactionnelle de l'énergie de transfert dépend essentiellement de la solvatation du groupement fonctionnel de la molécule d'acide et cette comparaison permet éventuellement une estimation de sa valeur dans différents solvants.

SUMMARY

The ion transfer in general and the proton transfer in particular are discussed in view of a theory of acidity and the importance of the energy of transfer is shown. This energy consisting of an intrinsic and an interactional part, is analysed and stress is laid upon the fact that the interactional part cannot, in general, be a simple function of the dielectric constant of the solvent. The intrinsic part may, on the other hand, be easily compared in different solvents. The energy of transfer enables one to define a universal acid-strength function X which has a precise physical meaning. The comparison of this function X in different solvents shows that the interactional part of the energy of transfer depends essentially on the solvatation of the functional group of the acid's molecule and permits eventually an estimation of this part in different solvents.

ZUSAMMENFASSUNG

Der Ionentransport im Allgemeinen und der Protonentransport im Besonderen werden als Grundlage einer Theorie der Azidität erörtert und die Wichtigkeit der Transportenergie wird aufgezeigt. Diese Energie besteht aus einer sogenannten ,,inneren" und einer sogenannten ,,Wechselwirkungs"-Energie; letztere kann im allgemeinen keine einfache Funktion der dielektrischen Konstante des Lösungsmittels sein. Dagegen lassen sich die inneren Energien in verschiedenen Lösungsmitteln leicht vergleichen. Auf Grund der Transportenergie kann man eine universelle Säure-Stärke-Funktion X definieren die eine genau umschriebene physikalische Bedeutung hat. Der Vergleich der Werte dieser Funktion in verschiedenen Lösungsmitteln zeigt, dass die Wechselwirkungs-Energie im Wesentlichen von der Solvatierung der funktionellen Gruppe des Säuremoleküls abhängt, und ermöglicht schliesslich eine Schätzung dieser Energie in verschiedenen Lösungsmitteln.

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THE BEHAVIOUR OF SOME METAL ANTHRANILATES IN BUFFERED SOLUTIONS

by

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INTRODUCTION

Anthranilic acid and certain related compounds such as 5-bromoanthranilic acid have long been used as precipitating agents in inorganic analysis. Their widest use is as gravimetric reagents, although volumetric methods have been suggested, for example by CIMERMAN AND SELZER[1] and HOLMES AND CRIMMIN[2], the latter giving in addition an absorptiometric method for completing the determination.

It has been suggested that anthranilic acid might be used as a reagent for metal ions in qualitative analysis. In view of this, and because the metal anthranilates were of interest to us in another connection, it was thought desirable to study the behaviour of the acid with metal ions, and in particular the sensitivity of the reactions.

Many definitions of the efficiency of a reagent as a precipitant for metal ions have been put forward since that of LUTZ[3] in 1920. The most systematic is that of IRVING, BUTLER AND RING[4] who studied the precipitating properties of reagents under strictly controlled conditions, regulating the pH of the solutions by means of buffers. To express their results they used a sensitivity exponent pL defined by pL = $-\log_{10}$ (limiting concentration, in gram-equivalents per litre, of metal ion which forms a precipitate under the conditions of the experiment).

What may be called the 'visibility' of the precipitate plays an important part in evaluating pL, and IRVING and his co-workers found it expedient to give an upper and a lower limit for the pL value, the latter corresponding to the largest amount of metal ion to give no visible precipitate.

This symbol differs from that of the International Union which has introduced the term pD, defined in a similar manner, but in terms of milligrams per ml instead of gram-equivalents per litre. In this paper pL will be used, although it will be re-defined as pL = $-\log_{10}$ (limiting concentration, in gram-atoms per litre, of metal ion which forms a precipitate under the conditions of the experiment).

IRVING determined sensitivities in the following buffers:

A. 250 ml of 2*N* acetic acid, 225 g of sodium acetate trihydrate, and 500 ml distilled water. pH = 5.2

B. 40 ml of 2*N* ammonium hydroxide, 320 g of ammonium acetate, 30 g of sodium potassium tartrate and 850 ml of distilled water. pH = 8.4

C. 500 ml of 2*N* sodium hydroxide, 275 g of sodium potassium tartrate and 500 ml of distilled water. pH = 12.4

It is known that most metal anthranilates are soluble in strong acetate solutions. This might have an affect on the pL values obtained and to investigate such a possibility acetate buffers rather different from the above were used.

EXPERIMENTAL

pL values were determined as originally described by IRVING except for the variation in buffers.

Reagent solutions

Standard solutions of the metal ions were prepared from AnalaR or Specpure materials.

The anthranilic acid solution was 0.1*M* in water and adjusted to a pH of 7.0 with sodium hydroxide solution.

Buffer solutions

A. 20 g anhydrous sodium acetate per litre, adjusted to a pH of 5.20 with acetic acid.
B. 200 g anhydrous sodium acetate per litre, adjusted to a pH of 5.20 with acetic acid.
C. 20 g anhydrous sodium acetate per litre, adjusted to a pH of 7.00 with acetic acid.
D. Sodium potassium tartrate buffer of pH identical with that of IRVING.
U. pL values were also determined in unbuffered solution, the buffer being replaced by an equivalent volume of water.

RESULTS AND DISCUSSION

The results obtained are recorded in Table I, only the higher value of pL being given. The highest concentration of metal ion solution used was 1 mg per ml. If no value was given at this concentration, then N.P. is recorded in the table.

TABLE I

Metal	*Buffer*				
	A	B	C	D	U
Ag^+	1.6	1.6	1.6	—	1.6
Al^{+3}	N.P.	N.P.	N.P.	—	N.P.
Be^{+2}	N.P.	N.P.	N.P.	—	N.P.
Cd^{+2}	3.0	2.0	2.8	—	3.6
Co^{+2}	3.0	2.0	3.0	—	3.6
Cu^{+2}	4.5	4.5	4.5	—	4.7
Fe^{+3}	—	—	—	—	
Hg^{+2}	—	—	—	—	4.2
Ni^{+2}	3.4	2.4	3.4	—	3.9
Zn^{+2}	2.7	2.1	3.3	—	3.7

Notes

a) In buffer D the result, in general, was no different from the blank.

b) Silver anthranilate was found to decompose at the temperature of the water bath and the sensitivity determination was carried out at room temperature.

c) In the cases of both ferric and mercuric ions only unbuffered solutions proved suitable for determinations.

The pH's of the unbuffered solutions were measured after the removal of the precipitate by centrifuging. They varied little from neutrality; in the cases of copper, cobalt and nickel, for example, they were 7.0, 6.7 and 6.8 respectively. Thus results from unbuffered solutions may be compared directly with those from buffer C, and when this is done it can be seen that, with the exception of Cu^{+2} and Ag^+, all the metals for which figures are given are less sensitive in buffered than in unbuffered solution; the increased solubility in the buffer must be due to the additional ions present. This is further borne out by comparison of pL values in buffers A and B, where the sensitivity of the reagent for some metals is appreciably less in the stronger buffer.

In general buffers A and C show little difference in result; this is to be expected since both lie within the pH range of complete precipitation of anthranilates.

In the case of anthranilic acid and other substances which behave similarly, no exact conclusions may be drawn from sensitivity measurements in one set of conditions as to the worth of the reagent when used in other conditions, although in some instances the use of acetate buffers weaker than those of IRVING may be helpful in that they are nearer to normal analytical practice. Sufficient buffering effect seems to be given with such weaker buffers; with buffers A and C and the given anthranilic acid reagent, the pH's of the solutions after precipitation were found to be little removed from those expected, although when anthranilic acid dissolved in ethanol was used the variation was greater. It would appear a wise precaution with weaker buffers to use a neutral solution of the sodium salt of the precipitating agent, when this latter is appreciably acidic, rather than a solution in an organic solvent.

The common features of behaviour in the different buffers may be summarized as follows:

a) A smaller sensitivity in buffer B than in buffer A due to the increased acetate concentration; sometimes the decrease was appreciable. The exceptions to this were copper, the anthranilate of which is known to be insoluble in acetate solution, and silver.

b) A smaller sensitivity in a buffered solution of pH 7 than in an unbuffered one of approximately the same pH. Once more copper and silver were exceptional, so that silver anthranilate must also be insoluble in acetate solutions.

To show that these effects were not limited to acetate buffers, two buffers were prepared of as nearly as possible the same molarity and pH but of different type. These were sodium acetate-acetic acid and potassium hydrogen phthalate-sodium hydroxide, both of pH 5.2. The amounts of these buffers necessary to prevent the precipitation of metal anthranilates was found. 4.2 ml of metal nitrate solution was added to different volumes of buffer, followed by 0.2 ml of 0.1*M* neutralized anthranilic acid solution. The total volume was adjusted to 9.2 ml with distilled water and the solution examined for a precipitate after heating and cooling as in the sensitivity measurements. The amount of buffer necessary just to prevent precipitation was found in this way for different amounts of metal ion. Typical results in the cases of zinc and cobalt are given in Fig. 1.

It will be seen that in both buffers zinc anthranilate is the more soluble, and that for each metal the phthalate buffer inhibits precipitation much more strongly than does the acetate buffer.

pH's of incipient precipitation

GOTO[5] has given the pH's of incipient precipitation of some metal anthranilates. These values were obtained while using acetate buffers and hence, as has been pointed out by SHENNAN, SMITH AND WARD[6], doubt must be cast on the value of the data. We have re-determined the figures, in the absence of acetate ions, by the method of FLECK AND WARD[7]. In an investigation of the gravimetric determination of zinc and cadmium using anthranilic acid, FUNK[8] has found that, although results were low in the presence of sodium or potassium acetate, the presence of alkali metal chloride, sulphate or nitrate had little effect, except for cadmium with chloride ion, when very low results were obtained. We thought it wise, however, to obtain our values using both nitric and hydrochloric acid. Our results are given in Table II, together with those of GOTO.

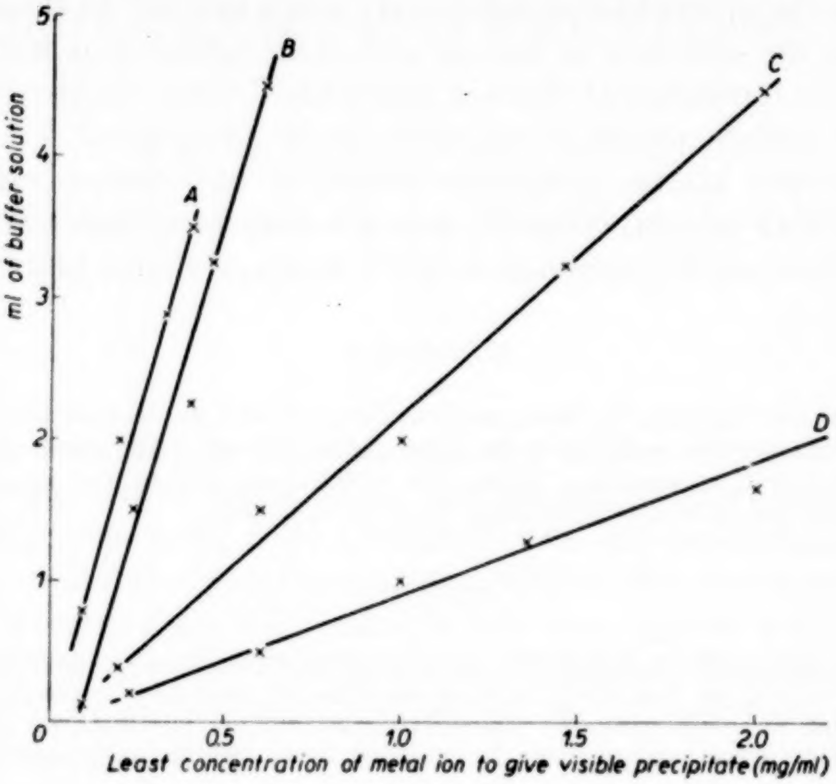

Fig. 1. A. Acetate buffer with zinc
B. Acetate buffer with cobalt
C. Phthalate buffer with zinc
D. Phthalate buffer with cobalt.

TABLE II

PH'S OF INCIPIENT PRECIPITATION

Metal ion	*pH using HNO_3*	*pH using HCl*	*pH obtained by* GOTO
Cu^{+2}	1·5	1·5	1·40
Ni^{+2}	2·0	—	3·64
Co^{+2}	2·6	2·8	3·36
Zn^{+2}	3·1	3·2	3·76
Pb^{+2}	3·4	3·5	—
Cd^{+2}	3·5	3·1	4·25
Mn^{+2}	3·8	3·8	4·10

Note: it was difficult to obtain a precise figure with nickel using hydrochloric acid.

In all cases except that of copper, which is known to be insoluble in acetate solution, the pH's are less than those given by GOTO.

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CONCLUSIONS

Holmes and Reed[9] have shown that anthranilic acid chelates react only very weakly with metal ions; copper anthranilate is the only one with an overall stability constant greater than four, the others having values very much smaller. In these circumstances it is possible that the solubility in acetate and other similar ions from weak acids is due to competitive formation of the not well ionised salts. Copper, forming a more strongly bonded chelate would be expected to be exceptional.

In view of the well known anomolous behaviour of cadmium chloride solutions (see for example Harned and Owen[10]) it is not surprising that the pH of incipient precipitation is different for cadmium in nitric acid and hydrochloric acid solutions.

SUMMARY

The sensitivity of the reaction between anthranilic acid and metal ions has been determined. The effect of the acetate buffer is found to be appreciable, except in the cases of copper and silver, but not large. Other buffers similarly affect the results, decreasing the sensitivity. The pH's of incipient precipitation of the anthranilates have been found.

RÉSUMÉ

Les auteurs ont déterminé la sensibilité des réactions entre l'acide anthranilique et certains ions métalliques. L'effet d'un tampon à l'acétate est sensible, sauf dans le cas du cuivre et de l'argent, mais pas grand. D'autres tampons affectent également les résultats, en diminuant la sensibilité. Les pH de début de précipitation des anthranilates ont été déterminés.

ZUSAMMENFASSUNG

Die Empfindlichkeit der Reaktion zwischen Anthranilsäure und verschiedenen Metallionen wurde untersucht. Der Einfluss des Acetatpuffers ist ausser im Falle von Kupfer und Silber merkbar, aber nicht gross. Andere Puffer haben einen ähnlichen Einfluss indem sie die Empfindlichkeit vermindern. Die pH-Werte bei denen die Fällung der Anthranilate beginnt, wurden ermittelt.

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THE RAPID SEPARATION AND DETERMINATION OF RADIOSTRONTIUM AND RADIOCAESIUM IN FISSION PRODUCT MIXTURES

by

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A technique has been described[1] for precipitating cations and removing them from solution without the use of filtration or centrifugation, by passing the solutions through anion exchange resin beds saturated with the precipitating anion. The precipitate forms around the resin beads as an adhering film, and the eluate from the column is clear. More recently the technique has been applied with success to the precipitation of radioactive tracers in the carrier-free state[2]. Employing a column in the hydroxide form the authors have removed all the activity from an aged fission product solution with the exception of that due to radiostrontium and radiocaesium. Any anionic activity was removed by normal ion exchange processes, while all the other long-lived cationic activity was precipitated on the hydroxide column. Separation of the strontium and caesium in the eluate was then carried out prior to the precipitation of each element in a form suitable for counting after gravimetric determination of chemical yield. By this means the determinations of these two elements were accomplished more rapidly and with better precision than by existing procedures[3]. Under conditions of routine use, 8 determinations of each radioelement were made simultaneously in under 2 days per operator and the precisions obtained (3σ for about 30 results) were 10% for strontium and 8% for caesium.

EXPERIMENTAL

Aliquots of fission product solution (at least several months old and therefore containing very little ^{140}Ba (12.8d)) with added known amounts of caesium and strontium carriers were passed down columns of Amberlite IRA-400(OH) and eluted with several column volumes of water. The eluates were heated almost to boiling and saturated ammonium oxalate was then added to precipitate the strontium. The precipitates were centrifuged off, washed several times with water, dried, weighed and counted. After correcting to 100% chemical yield, the results showed a good accuracy and precision.

The supernatant solutions from the oxalate precipitations were made about $5M$ in hydrochloric acid and an $0.1M$ solution of silicotungstic acid was added to precipitate the caesium. This again was centrifuged off, washed, dried, weighed and counted. Many of the sources became discoloured on drying, and this discoloration was associated with poor agreement among the results from the individual sources. It appeared that the caesium silicotungstate was unsuitable as a method of gravimetric determination. Several other reagents were considered (*e.g.* see reference[4]), but eventually it was decided to employ perchloric acid[5]. The solution had to be free from any ammonium ion during this precipitation of caesium, because ammonium perchlorate also precipitates under the conditions used. Therefore, either the ammonium oxalate used in the precipitation of strontium had to be volatilized, or else the caesium and strontium had to be separated without the use of ammonium oxalate. The removal of ammonium oxalate by volatilization was avoided as it would prove time consuming, and a rapid separation was being sought. Using a column of anion exchange resin in the oxalate form, the strontium could be removed from the caesium without the introduction of any cation which would interfere in the subsequent precipitation of caesium as perchlorate. However, the strontium carrier immediately precipitated as a pad on top of the resin, and this slowed down the column flow-rate to such an extent that it made its use in a routine method impracticable.

A much simpler and more rapid separation was effected by the addition of carbon dioxide (in the solid state for convenience) to the eluate from the hydroxide column. Thus the strontium was removed quantitatively without the addition of any interfering cation. The caesium could then be precipitated as perchlorate, while the strontium carbonate was dissolved in acid and the strontium reprecipitated as oxalate.

Analysis of the strontium sources by β-absorption measurements showed the activity to be entirely due to ^{89}Sr, ^{90}Sr and ^{90}Y. The last-named isotope begins to grow in from its ^{90}Sr parent after chemical separation has occurred. Only negligible traces of γ-activity were observed in the sources. γ-spectrometric analysis of the caesium sources showed them to be more than 99% ^{137}Cs/^{137m}Ba with a trace of ^{134}Cs.

Reagents

Strontium carrier solution (9.5 g $SrCl_2 \cdot 6H_2O$ in 100 ml water).

Caesium carrier solution (2.75 g CsCl in 100 ml water).

(The strontium and caesium contents of the respective solutions should be determined accurately by normal gravimetric procedures.)

Carbon dioxide (solid or from Kipp's Apparatus).

Procedure

The columns should be 40-50 cm long, 1.2-1.4 cm internal diameter and should contain 8-10 g Amberlite IRA-400(OH) resin. Before use, wash the columns with about 50 ml of 4*M* nitric acid to remove any retained activity from previous experiments. Remove the excess of acid with water, then pour through the columns a strong sodium hydroxide solution prepared from carbon-dioxide-free distilled water. Fit an absorption tube containing soda-lime in the top of each column. Remove the excess of sodium hydroxide by washing.

Pipette an aliquot of the solution for analysis, which should contain negligible amounts of ^{140}Ba into a small beaker and add 2.0 ml of both caesium and strontium carrier solutions. The aliquot should be chosen to contain quantities of activity suitable for counting. The ^{89}strontium activity should be between 3×10^3 and 1.5×10^6 disintegrations per minute and the ^{137}caesium activity 2×10^4 to 6×10^5 d.p.m. In addition, the aliquot should not contain more than four milliequivalents of anion other than hydroxyl, otherwise the effectiveness of the column may be impaired owing to replacement of the hydroxyl ions by other non-precipitating anions.

Transfer the solution and washings into the column and allow the liquid to flow through slowly at a rate of 0.5-1 ml per minute. Collect the eluate in a 150 ml beaker, and when the liquid level in the column has almost reached the level of the resin, add distilled water. Continue the elution until about 40 ml has been collected, then precipitate the strontium with carbon dioxide. (If solid carbon dioxide is being used add 1-2 g.) Centrifuge off the precipitate and dissolve it in a little dilute hydrochloric acid and dilute to about 20 ml with water. Retain the supernate from the precipitation for the determination of caesium.

Boil the strontium solution to expel any carbon dioxide, cool, add 2 ml of 18*M* ammonium hydroxide and heat again almost to boiling. Slowly add 5 ml of saturated ammonium oxalate solution, and allow the beaker and its contents to cool. Centrifuge off the precipitate, wash it several times with water and then transfer it as a slurry with acetone to a weighed stainless steel or glass counting tray. Dry the precipitate carefully, weigh it and count the source without delay.

Standard G.M. counting equipment with a total absorber thickness of 130-140 mg/cm² should be used. Thus the 0.6 MeV β-activity of ^{90}Sr is absorbed and only the 1.5 MeV β-emission of ^{89}Sr is counted. However, ^{90}Y the daughter element of ^{90}Sr commences to grow in with a half-life of 61 hours immediately after elution from the column, and the energy of its β-radiation is 2.2 MeV. The time interval between the column separation and the counting should therefore be noted. Recount the sample several days later, using the same equipment, and note the time of counting. Correct the counts for counting efficiency, background, back-scatter and self-absoption as necessary. Calculate the fraction of the total ^{90}Y which has grown in during the interval between the first and second countings, and hence find the ^{90}Sr activity. The amount of ^{90}Y activity present during the first counting is therefore known, and by difference calculate the ^{89}Sr activity.

Fume down the supernate containing the caesium with 6 ml of 9*M* perchloric acid. After fuming has continued for 10 minutes, cool the mixture in a 50 ml centrifuge tube in an ice-bath. Add 15 ml of absolute alcohol and allow to stand for 10 minutes, stirring occasionally. Centrifuge

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off the precipitate, wash it several times with absolute alcohol and transfer it as a slurry with acetone to a weighed stainless steel or glass counting tray. Dry under a radiant heater, weigh and count the source.

Standard γ-scintillation counting equipment fitted with a 2 g/cm^2 absorber of lead and aluminium (to prevent formation of Bremmstrahlung) should be used. The γ-rays are actually emitted by ^{137m}Ba, the meta-stable daughter, which has a half-life of 2.6 minutes and therefore quickly reaches equilibrium. Corrections are made for counting efficiency (including the absorber) and also for the fact that only 82.5% of the total ^{137}Cs disintegrations produce γ-rays from ^{137m}Ba, the rest being lost either by direct decay to stable ^{137}Ba, or else by interval conversion of the γ-rays[6].

Note added in proof

During the routine use of this method for strontium analysis a very small variable positive bias was encountered. Following a discussion with FUDGE AND JENKINS of A.E.R.E. Harwell, special attention was directed to the behaviour of cerium.

A high activity run was carried out and following precipitation of strontium carbonate the strontium was precipitated from fuming nitric acid. A small amount of 141 cerium was identified remaining in solution on analysis by β-absorption curve. It is believed that formation of a radiocolloid is the cause of the solution of a small variable proportion of the cerium in the sample. The addition of 10 mg of cerium carrier (as cerous nitrate) before column treatment has been proved to prevent elution of the radiocerium, and the bias was removed from the method. (A paper by FUDGE AND JENKINS on their work with column precipitation will be published shortly.)

ACKNOWLEDGEMENTS

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SUMMARY

Anion exchange columns in the hydroxide form have been used to remove all fission products from solution except strontium and caesium (assuming barium absent). These two elements have been determined in the eluate by precipitation of oxalate and perchlorate respectively. The resulting procedure has been found to be more precise and quicker than others previously used.

RÉSUMÉ

Des colonnes d'échangeurs d'anions, sous forme d'hydroxyde, ont été utilisées pour éliminer tous les produits de fission de la solution à l'exception du strontium et du césium (le baryum étant absent). Ces deux éléments ont été dosés dans l'éluat par précipitation comme oxalate et perchlorate, respectivement. Ce procédé semble plus précis et plus rapide que d'autres déjà utilisés.

ZUSAMMENFASSUNG

Anionenaustauschersäulen in der Hydroxyd-Form wurden zur Entfernung aller Spaltprodukte mit Ausnahme von Strontium und Caesium aus der Lösung angewendet. (Hierbei wird angenommen dass Barium abwesend ist.) Diese beiden Elemente wurden im Eluat durch Fällung als Oxalat und resp. als Perchlorat bestimmt. Dieses Verfahren ist genauer und rascher als andere, früher beschriebene Verfahren.

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DIETHYLENETETRA-AMMONIUM SULPHATOCERATE AS VOLUMETRIC REAGENT

III. FERROUS ETHYLENEDIAMINE SULPHATE METHOD

by

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Diethylenetetra-ammonium sulphatocerate reacts with ferrous ethylenediamine sulphate, $FeSO_4.(CH_2.NH_3)_2SO_4.4H_2O$, in acid medium according to the following equation:

$$Ce^{+4} + Fe^{+2} = Ce^{+3} + Fe^{+3}$$

In the present investigation sodium oxalate, hydrogen peroxide, potassium thiocyanate, ferrous ammonium sulphate, cuprous chloride and hydroquinone have been determined indirectly using diethylenetetra-ammonium sulphatocerate as an oxidant. The excess of standard diethylenetetra-ammonium sulphatocerate solution added to each of the substances was titrated back with standard ferrous ethylenediamine sulphate solution.

EXPERIMENTAL

A known weight of each substance was mixed with an excess (25-30 ml) of 0.02*N* diethylenetetra-ammonium sulphatocerate solution and the mixture acidified with sulphuric acid to keep its normality between 1 and 2*N*. The mixtures containing sodium oxalate, potassium thiocyanate and cuprous chloride were heated to complete the reaction and then allowed to cool. In case of cuprous chloride, 10 ml of 3*N* HCl were also added to the mixture. In each case the excess diethylenetetra-ammonium sulphatocerate was titrated potentiometrically and volumetrically against 0.02*N* ferrous ethylenediamine sulphate solution at 20° C.

In the potentiometric method, the mixture was kept stirred by a mechanical stirrer during the titrations. A bright platinum foil immersed in the solution to be titrated was used as an oxidation-reduction electrode, and this was coupled with a saturated calomel electrode through an agar-agar potassium chloride bridge. During the titration the progress of the reaction was studied potentiometrically. At the equivalence point a sharp jump in potential was observed in each titration. A series of potentiometric titrations were performed with different amounts of each substance. The titrations, one for each substance, are represented by the curves, A to F, given in Fig. 1.

In case of the volumetric method, the excess of diethylenetetra-ammonium sulphatocerate solution added to each substance was titrated back with the standard ferrous ethylenediamine sulphate solution, using ferroin as an indicator.

From the volume of the ferrous ethylenediamine sulphate used, corresponding to the equivalence point in each titration, the amount of diethylenetetra-ammonium sulphatocerate required for the oxidation of each substance was calculated and consequently the amount of each substance was determined. The results showed that 0.110 to 0.560 meq. of the substances as listed above can be determined indirectly by using diethylenetetra-ammonium sulphatocerate as an oxidizing agent.

All chemicals used in this investigation are of guaranteed purity. Diethylenetetra-ammonium sulphatocerate (DTS) was prepared by the method of B. SINGH *et al.*[1]. The standard solution of diethylenetetra-ammonium sulphatocerate was prepared by dissolving its known weight in 2*N* sulphuric acid solution and making to a known volume with the acid. Ferrous ethylenediamine sulphate (FES) was prepared by the method of CARAWAY AND OESPER[2].

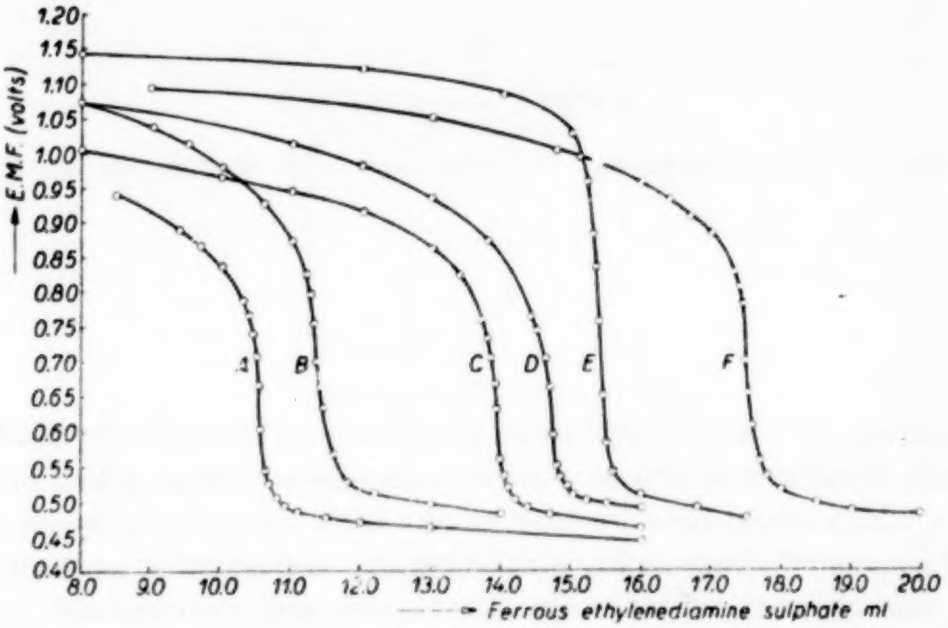

Fig. 1. Curve A $(COONa)_2$ Curve D $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
Curve B H_2O_2 Curve E Cu_2Cl_2
Curve C KCNS Curve F $C_6H_4(OH)_2$

SUMMARY

Diethylenetetra-ammonium sulphatocerate has been used as an oxidizing agent in 2*N* sulphuric acid for the indirect determinations of sodium oxalate, hydrogen peroxide, potassium thiocyanate, ferrous ammonium sulphate, cuprous chloride and hydroquinone. An excess of standard diethylenetetra-ammonium sulphatocerate added to each of the substances is titrated potentiometrically as well as volumetrically with a standard solution of ferrous ethylenediamine sulphate.

RÉSUMÉ

Le sulfate de di-(éthylènediamino)-cérium(IV) a été utilisé comme oxydant, en milieu sulfurique 2*N*, pour les dosages indirects de l'oxalate de sodium, du peroxyde d'hydrogène, du thiocyanate de potassium, du sulfate double de fer (II) et d'ammonium, du chlorure de cuivre(I) et de l'hydroquinone. L'excès de solution étalon du réactif ajoutée à chacune de ces substances, est titré soit potentiométriquement, soit volumétriquement par une solution étalon de sulfate double de fer(II) et d'éthylènediamine.

ZUSAMMENFASSUNG

Das Cer(IV)-di(äthylendiamin)-sulphat wurde als Oxydationsmittel in 2*N* Schwefelsäure zur indirekten Bestimmung von Natriumoxalat, Wasserstoffperoxyd, Kaliumthiocyanat, Eisen(II) ammoniumsulphat, Cuprochlorid und Hydrochinon verwendet. Eine Titerlösung des Reagenzes wird im Überschuss zu jeder dieser Substanzen gefügt und dann potentiometrisch oder volumetrisch mit einer Titerlösung von Eisen(II)-äthylendiamin-sulphat zurücktitriert.

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LOPHINE, A NEW CHEMILUMINESCENT INDICATOR

by

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The application of chemiluminescent indicators in volumetric analysis enables us to carry out titrations in turbid, dark or coloured solutions, which were previously impossible or which could only be carried out with the aid of instruments. KENNY AND KURTZ[1] suggested siloxene for indicating the end-point of redox-titrations and luminol for acid-base titrations[2]. PONOMARENKO and co-workers[3] improved the method, employing less luminol. On further investigation of analytical applications of chemiluminescent indicators and new indicator reactions we found lucigenine and luminol suitable for indicating the end-point of redox-titrations performed in basic medium[4]. We found lucigenine to be a reversible acid-base indicator[5]. Further investigations of ours showed that lophine (2.4.5-triphenylimidazole), which is easily prepared, is a good indicator for acid-base titrations. Its use will be reported as follows.

Lophine was first produced by LAURENT[6] and its chemiluminescence was described by RADZISZEWSZKI[7]. Our product was prepared according to the latter's directions[8], by saturating the alcoholic solution of benzil and benzaldehyde (1 + 1 mole) with ammonia. The 0.4% alcoholic or 1% acetonic solution of lophine was used as indicator.

Atmospheric oxygen alone produces a light emission in a solution of great quantities of lophine in concentrated alcoholic potassium hydroxide[7]. To obtain a light emission from a single drop of $0.1N$ base, a little dilute hydrogen peroxide should be added to the solution. The active oxygen delivery was accelerated by a small quantity of potassium ferricyanide. Approaching the end-point of the titration, a precipitation of lophine might easily have been formed in the aqueous solution, so ethanol was added to the solution of the acid to be titrated. In the darkness, bright flashes are observed during titration, where the base drops in. At the end-point the solution emits light steadily for at least one minute. The titration of bases may be adequately performed by back-titrating, adding a measured excess of acid to the solution and titrating with basic volumetric solution in the presence of lophine, hydrogen peroxide and potassium ferricyanide. The determination may also be carried out by titrating a known quantity of acid volumetric solution with the base to be determined.

In order to determine the pH-range of chemiluminescence of the indicator we performed potentiometric titrations, using a glass indicator and saturated calomel reference electrode. The titration curve is plotted in Fig. 1. Our indicator began to give light between 8.9 and 9.4 pH units and on increasing the pH-value the chemiluminescence becomes rather intense. In the case of considerable over-titration, precipitation of lophine could be observed, particularly if the quantity of the potassium ferricyanide had been increased.

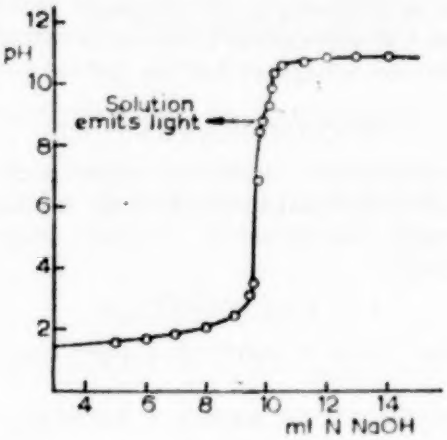

Fig. 1. Titration of 9.60 ml *N* HCl with *N* NaOH.

In view of these experiments we found our indicator to be suitable, as is phenolphthalein, both for the titration of strong and weak acids and for the titration of strong bases (by the method of back-titration).

The sensitivity of the indicator for carbon dioxide is similar to that of phenolphthalein, therefore a carbonate-free base should be used for the titration of weak or dilute strong acids. The addition to the volumetric solution of single drops can be facilitated by using a special buret adjusted with a buffer-plate[9].

Recommended procedure

To a weighed sample of acid at least 30 ml acid-free ethanol should be added per 100 ml end-volume. After adding 5 ml of 3% hydrogen peroxide, 1 ml of 5% potassium ferricyanide and 1 ml of 0.45% alcoholic or 1% acetonic solution of lophine, the solution is titrated with 1*N* or 0.1*N* sodium hydroxide volumetric solution in the dark, until the chemiluminescence observed at first only where the base drops in, extends to the whole liquid and lasts for at least one minute. The accuracy may be judged from the data of Table I. The determinations can be performed with an accuracy of 1-2% on the 0.1*N* scale.

TABLE I

Portions of 1N HCl	*Volume of 1N NaOH, equivalent to former portions of 1N HCl*	*Mean*	*Deviation from mean*	
ml	*ml*	*ml*	*ml*	%
5.02	5.05 5.04 5.03	5.04	+0.02	+0.4
10.00	9.94 10.02 10.04	10.00	±0.0	±0.0
20.08	20.09 20.13 20.06	20.09	+0.01	+0.05
30.12	30.12 30.18 30.17	30.16	+0.04	+0.1

SUMMARY

Lophine, a new chemiluminescent indicator, is suitable for marking the end-point of acid-base titrations. The indicator emits light in basic medium and in the presence of an oxidant and a catalyst. Lophine indicates the end-point in the same pH-range as phenolphthalein.

RÉSUMÉ

La lophine, nouvel indicateur luminescent, est proposée pour la détermination du point final des titrages alcali-acidimétriques. Cet indicateur émet de la lumière en milieu basique, en présence d'un oxydant et d'un catalyseur. Le virage se fait au même pH que celui de la phénolphtaléine.

ZUSAMMENFASSUNG

Lophin, ein neuer chemilumineszenter Indikator, eignet sich dazu, den Endpunkt von Säure-Basen-Titrationen anzuzeigen. Der Indikator leuchtet in basischem Medium und in Gegenwart eines Oxydationsmittels und eines Katalysators. Lophin zeigt den Endpunkt in demselben pH-Bereich an wie Phenolphtalein.

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SUR LE DOSAGE DE L'ATOPHAN

par

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Pour le dosage de l'atophan A. CASTIGLIONI[1] avait proposé l'emploi de l'acide silicotungstique, qui précipite l'atophan en solution chlorhydrique comme silicotungstate.

L'éventuelle présence des acides salicylique et acétylsalicylique ne gêne pas le dosage, on obtient alors un précipité contenant à l'état libre les acides salicylique et acétylsalicylique, tandis que l'acide phényl-2 quinoléine carboxylique-4 (atophan) sera combiné à l'acide silicotungstique. Par calcination d'un tel précipité, on élimine les acides salicylique et acétylsalicylique et on obtient un résidu d'anhydride silicotungstique correspondant à l'acide phényl-2 quinoléine carboxylique-4.

La même réaction a permis à A. MOREL[2] de doser l'atophan en déterminant par colorimétrie, ay moyen de chlorure de titane(II), l'acide silicotungstique resté libre après la précipitation de l'atophan.

D'autre part, nous avons remarqué que le molybdate d'ammonium peut précipiter quantitativement l'atophan des solutions de ses sels, acidifiées par l'acide acétique.

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Dans nos conditions expérimentales, les acides salicylique et acétylsalicylique ne précipitent pas. Ainsi, même en leur présence, le composé atophan-acide molybdique peut être séparé, séché et pesé.

A un tel composé on peut attribuer la formule:

$$C_{16}H_{11}O_2N \cdot 2MoO_3 \cdot H_2O$$

On peut calculer la teneur en atophan en multipliant le poids du précipité obtenu par 0.4488.

Dans le tableau qui suit on a donné quelques-uns des résultats obtenus.

Atophan (g)		
Théorique	*Trouvé*	*Erreur*
0.0533	0.0521	—0.0012
0.0517	0.0516	—0.0001
0.0510	0.0517	+0.0007
0.0508	0.0515	+0.0007

Pour la détermination analytique on peut procéder de la manière suivante:

On prépare la solution des trois acides en employant un léger excès d'hydroxyde d'ammonium et on complète à un volume donné.

On prélève 10 ml de cette solution et on les ajoute goutte à goutte à 20 ml de solution aqueuse de molybdate d'ammonium à 2%, additionnée de 10 ml d'acide acétique glacial; on porte à l'ébullition.

On obtient un précipité gélatineux constitué uniquement par le composé atophan et acide molybdique; on chauffe au bain-marie pendant quatre heures environ, de façon que ce précipité devienne granulaire, et facile à filtrer. On filtre et on lave avec 250 ml environ de solution d'acide acétique à 10%, jusqu'à élimination totale des ions molybdiques; on sèch à 105° et on pèse; le poids obtenu multiplié par 0.4488, donne la teneur en atophan.

RÉSUMÉ

Les auteurs proposent une méthode de dosage de l'atophan en présence des acides salicylique et acétysalicylique, par précipitation avec le molybdate d'ammonium.

SUMMARY

A method is described, permitting the determination of atophan in the presence of salicylic and acetylsalicylic acids by precipitation with ammonium molybdate.

ZUSAMMENFASSUNG

Eine Methode zur Bestimmung von Atophan, in Gegenwart von Salicyl- und Acetylsalicylsäure, durch Fällung mit Ammoniummolybdat wird beschrieben.

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ZUR BESTIMMUNG DES GLÜHVERLUSTES VON TONERDEHYDRATEN

von

HEINZ WIELE

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Die direkte Bestimmung des Aluminiums in technischen Tonerdehydraten liefert Abweichungen gegenüber dem indirekt aus den Glühverlusten errechneten Aluminiumgehalt. Diese an sich bekannte Tatsache ist schon früher Gegenstand von Untersuchungen gewesen[1-5], findet aber heute noch keineswegs genügend Beachtung.

Wir konnten nun zeigen, dass es nicht zulässig ist, durch Differenzbildung aus der Bestimmung der Verunreinigungen und des Glühverlustes in der üblichen Art auf den Al_2O_3-gehalt von technischen Tonerdehydraten zu schliessen, weil bei der Ermittlung des Glühverlustes nach der gebräuchlichen Vorschrift[6] die Glühprodukte selbst nach Erhitzung auf 1200 bzw. 1350° C noch eine Hygroskopizität besitzen, die erhebliche Analysenfehler bewirkt.

Für die Modellversuche wurde reinstes Aluminium (99.993%) verwendet. Der nach der Auflösung des Metalles und Fällung mit Ammoniak bzw. Thiosulfat erhaltene Niederschlag wurde nach Filtration und sauberer Auswaschung verglüht; die Glühprodukte wurden über P_2O_5 im Exsikkator aufgehoben. Die Glühversuche wurden bei Temperaturen von 900 bis 1500° C in einem Kammerofen mit Silitstabheizung unter laufender Temperaturkontrolle durchgeführt; die Glühzeiten betrugen 1 bis 3 Stunden. In Kontrollversuchen waren die Platintiegel gesondert auf ihre Gewichtsabnahme nach Glühen bei den gleichen Temperaturen überprüft worden. Eine messbare wesentliche Abnahme des Gewichtes wurde erst ab 1300° C beobachtet. Daher wurden bei diesen Temperaturen und oberhalb nur keramische Tiegel aus Sinterkorund (Degussit-Masse Al 23) verwendet. Alle Wägungen wurden auf Halbmikro-Waagen durchgeführt.

Die Versuche lassen, wie aus Tabelle I hervorgeht, eine Abhängigkeit der Wasseraufnahme

TABELLE I

ABHÄNGIGKEIT DER H_2O-AUFNAHME VON DER ANGEWENDETEN Al_2O_3-MENGE NACH GLÜHUNG BEI KONSTANTER TEMPERATUR

Angewandte Menge Al_2O_3 in mg		4.5	8.5	18.7
Glühtemperatur 850° C, 15 Min.	Wägung nach Abkühlung über P_2O_5 in mg	4.85	9.15	19.30
1200° C, 15 Min.		4.70	8.80	19.10
1200° C, 30 Min.		4.45	8.50	18.70
Nach der letzten Wägung 15 Min. offen in der Waage stehen gelassen und erneut gewogen (mg)		5.30	9.75	19.80
Gewichtszunahme in mg		0.85	1.25	1.10
Gewichtszunahme in %		16.0	12.8	5.5

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nach der Glühung bei 1200° C von der Grösse der Einwaage erkennen. Man erhält aber andererseits nach 30 minütigem Glühen bei 1200° C und Abkühlen im Exsikkator über P_2O_5 die wirklich eingesetzten Mengen wieder unter der Voraussetzung, dass genügend schnell und mit bedeckten Tiegeln gewogen wird. Lässt man im Anschluss die geglühte Substanz an der Waage offen, z.B. 15 Min. stehen, so machte die erhebliche Gewichtszunahme, die durch Adsorption von Wasser eintrat, in dieser kurzen Zeit bereits eine exakte Bestimmung unmöglich. Der Fehler nimmt mit Grösserwerden der Einwaage relativ ab. Dieses Ergebnis liess erkennen, dass bei entsprechend grösseren Einwaagen, wie es bei der Bestimmung von Glühverlusten der Tonerdehydrate üblich ist, sehr lange Glühzeiten bei 1200° C notwendig wären, um überhaupt vergleichbare Ergebnisse zu erhalten. Den Beweis hierfür zeigt Figur 1. Bei Verwendung einer grösseren Einwaage von ca. 1 g Aluminium ist nach der Ausfällung als Hydroxyd, anschliessendem Verglühen bei 1200° C nach 2 Stunden und Abkühlen im Exsikkator über P_2O_5 noch so erhebliche Hygroskopizität vorhanden, dass kein konstanter Endwert ermittelt wird. Dies ist erst bei einer Glühtemperatur von 1500° C der Fall. Weitere Versuche zeigten, dass die Glühung von Tonerdehydraten mit grösseren Einwaagen bei Temperaturen um 1200° C nur dann reproduzierbare Werte liefert, wenn mit peinlicher Sorgfalt die schnell eintretende Wasseradsorption beim Auswägen ausgeschaltet wird. Dies kann nur erreicht werden durch Einstellen des noch heissen Tiegels in ein Quarzschliffgläschen unter sofortigem Verschliessen und Aufbewahren im Exsikkator über P_2O_5. Es genügt also nicht mehr das Aufbewahren allein im Exsikkator über P_2O_5 und einfach bedecktem Tiegel.

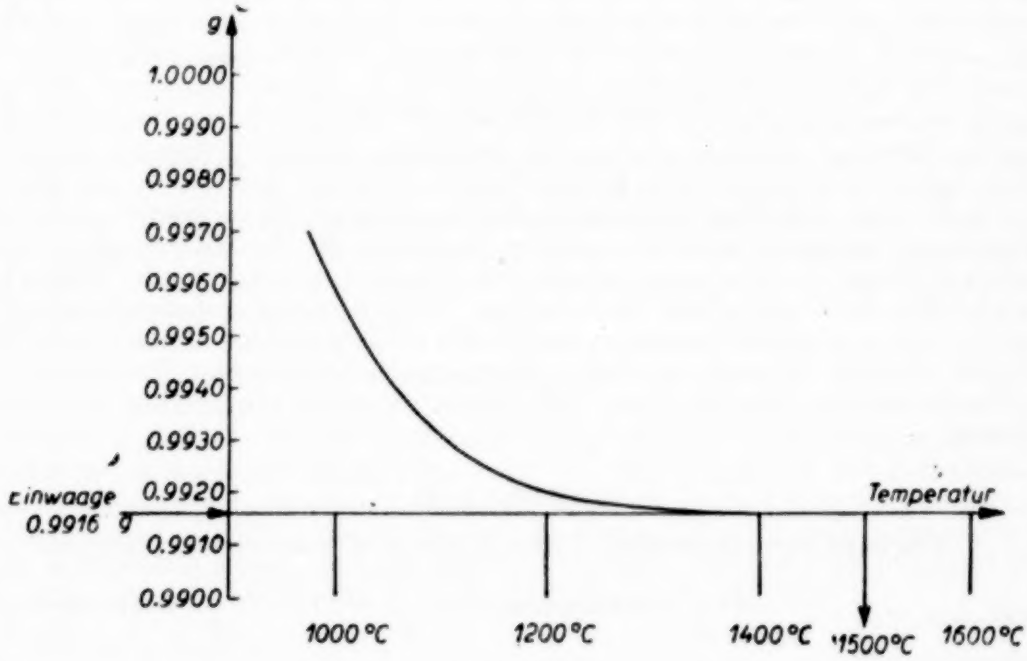

Fig. 1. Annäherung der als Al_2O_3 gefundenen und auf Aluminium berechneten Auswaagen an die angewendete Menge nach Glühung des Hydrates bei verschieden hohen Temperaturen. Einwaage: 0.9916 g Aluminium (1.8740 g Al_2O_3); Glühung jeweils 2 Stdn.

Die technischen Tonerdehydrate werden nun zumeist nach ihren Glühverlusten beurteilt, wobei für die Bestimmung Einwaagen von ca. 1-2 g Verwendung finden. In diesen Fällen müssen die oben beschriebenen Verhältnisse eine entscheidende Rolle spielen, in der Weise, dass zu niedrige Glühverluste gefunden werden. So zeigt der Versuch tatsächlich für eine Einwaage von 2 g Tonerdehydrat, Glühen (2 Stdn.) und Auswägung nach 30 bis 45 Min. folgende Gewichtszunahmen für die Glühprodukte, die dann auch bei längerem Aufbewahren (16 Stdn.) über P_2O_5 keine Änderung mehr erfahren:

Glühtemperatur °C	1100	1200	1300	1400	1500
Gewichtszunahme in %	4.5	1.25	0.5	0.2	0-0.05

Noch weit rascher verläuft die Adsorption von Feuchtigkeit beim Wägevorgang ohne Beachtung der Vorsichtsmassnahme der Wägung in geschlossenen Wägegläsern; man erhält keine Konstanz der Tiegelgewichte.

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Diese immer wieder beobachtete starke Adsorption von Feuchtigkeit findet ihre Deutung in den ausgeprägten oberflächenaktiven Eigenschaften des Aluminiumoxyds. Da die Oberflächenaktivität proportional von der Grösse der Oberfläche abhängt, bestimmten wir nach der Methode der Stickstoff-Adsorption von Brunauer, Emmett und Teller[7] in verschieden hoch geglühten technischen Tonerdehydraten die Oberflächengrösse und fanden für sie folgende Werte:

Glühtemperatur ° C	*Oberfläche m²/g*
1000	17.6
1250	8.3
1350	6.7
1500	3.8

(Die Oberflächenbestimmung wurde freundlicherweise von Herrn Dr. Hüdepohl durchgeführt).

Wie erwartet nimmt mit steigender Glühtemperatur die Oberfläche kontinuierlich ab und somit auch die Aktivität. Setzt man voraus, dass die Oberfläche im Al_2O_3 sich nur monomolekular mit Wassermolekeln bedeckt, so errechnet sich z.B. für 8.3 m² Oberfläche je g des Glühproduktes für 1250° C ca. 0.3% und für 6,7 m²/g entsprechend 1350° C ca. 0.20% Wasseraufnahme. Für 1500° C lässt sich ein Vergleich nicht heranziehen, da bei dieser Temperatur das Al_2O_3 weitgehend seine Adsorptionsfähigkeit verloren hat und nur noch geringste, allerdings messbare Wassermengen aufgenommen werden. In guter Übereinstimmung stehen diese Befunde mit den Ergebnissen einer erst vor kurzem erschienenen Arbeit von Carruthers und Gill[8], die mit Hilfe der Röntgenanalyse nachweisen konnten, dass erst bei 1720° C für das Aluminiumoxyd das Packungsmaximum in der Struktur durch Übergang des restlichen amorphen Anteiles des Oxyds in das Korund-Gitter unter Ausbildung von Kristallflächen erreicht und damit die kleinstmögliche Oberfläche erzielt wird. Die Oberflächenaktivität konvergiert dann gegen „null" hin.

Um die Ergebnisse weiter zu erhärten und den Nachweis der Gewichtszunahme durch Wasser auch auf anderem Wege zu erbringen, wurde die Fischer-Titration[9] zur Wasserbestimmung bei den verschieden hoch geglühten technischen Tonerdehydraten herangezogen. Zu diesem Zweck wurde in den geglühten Tonerdehydraten das aufgenommene Wasser nach der Fischer-Methode titriert. Tabelle II zeigt an zwei verschiedenen technischen Produkten, dass die so gefundenen Wassermengen durchaus mit den durch Wägung ermittelten Gewichtszunahmen übereinstimmten.

TABELLE II

TONERDEHYDRAT-PROBEN: 1060/4324/54 M UND 1060/4324/54 G

Glühtemperatur °C	*Gewichtszunahme mg*		*Wasser (titriert) mg*	
	M	*G*	*M*	*G*
1100	95.0	78.0	112.0	94.0
1200	24.4	20.1	26.2	21.0
1250	16.8	13.9	18.1	15.4
1300	10.6	8.5	10.8	8.2
1350	6.4	4.8	8.0	5.0
1400	3.2	2.6	2.4	2.4
1500	1.8	1.4	1.9	1.7

Für die Kontrollanalyse zur Betriebsüberwachung und noch mehr für die Schiedsanalyse erscheinen die Ergebnisse von besonderem Interesse. Die Zusammenstellung in Tabelle III zeigt, dass die nach 1/2 stündigem Glühen bei 1500° C und Abkühlen im Exsikkator über P_2O_5 erhaltenen Werte für den Glühverlust sehr gut mit der Differenz der einzeln bestimmten Verunreinigungen gegen 100 übereinstimmten, während die nach der sonst üblichen Vorschrift[6] ermittelten Glühverluste erheblich zu niedrig liegen.

Herrn Prof. Dr. P. W. Schenk danke ich für das rege Interesse, das er der Arbeit entgegenbrachte.

Den Herren W. Brokopf und H. Bluhm sage ich Dank für ihre tätige Mitarbeit und die gewissenhafte Durchführung der zahlreichen Analysen.

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TABELLE III

Bestandteil in %	1846/5044/53		1799/4850/53		1759/4736/53		1498/3988/53	
SiO_2	0.017		0.026		0.020		0.020	
Fe_2O_3	0.006		0.0093		0.009		0.0054	
Na_2O	0.018		0.012		0.015		0.026	
P_2O_5	0.002		0.002		0.002		0.002	
CaO	0.028		0.042		0.028		0.035	
Al_2O_3 (direkt)	64.86		64.80		64.88		64.82	
Summe der Komponenten	64.931		64.891		64.954		64.908	
Glühverlust bei 1250° C (wie bisher üblich)	34.66	Differenz zu 100% errechnet:	34.78	Differenz zu 100% errechnet:	34.70	Differenz zu 100% errechnet:	34.65	Differenz zu 100% errechnet:
Glühverlust bei 1500° C (gefunden)	35.10	35.07	35.10	35.11	35.03	35.05	35.00	35.09

ZUSAMMENFASSUNG

Es wird in Versuchen an reinen Aluminiumhydroxyd-Fällungen und technischen Tonerdehydraten gezeigt, dass die Verglühung zu Aluminiumoxyd bei 1200° C bis 1350° C nicht ausreichend ist und nur bei Einhaltung besonderer Vorsichtsmassnahmen zum Ziele führt, da die erhebliche Hygroskopizität des Glühproduktes schnell zur Wasseraufnahme führt. Erst bei 1500° C wird Gewichtskonstanz des entstandenen Aluminiumoxyds unter völliger Ausschaltung der Hygroskopizität durch „Totbrennen" erreicht.

SUMMARY

In experiments on pure aluminium hydroxide precipitations and technical hydrates of alumina it is shown that incandescing to aluminium oxide at 1200°-1350° C is not sufficient and is only successful when special precautions are taken. This is due to the fact that the considerable hygroscopicity of the product quickly leads to absorption of water. Only from a temperature of 1500° C onwards can a constant weight for the aluminium oxide produced be obtained by complete elimination of the hygroscopicity as a result of "dead-burning".

RÉSUMÉ

On démontre au moyen de précipités d'hydroxyde d'aluminium pur et d'argile hydratée technique, qu'une calcination de 1200° à 1350° C n'est pas suffisante pour une transformation complète en oxyde d'aluminium. Mais cela n'est possible que si l'on prend des précautions spéciales, car en raison de l'hygroscopicité notable du produit calciné, il y a rapidement une hydratation. C'est seulement à 1500° C que l'on atteint un poids constant de l'oxyde d'aluminium formé; on élimine totalement l'hygroscopicité par une calcination "à mort".

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THE USE OF ION EXCHANGERS FOR DETERMINING THE GRADE OF FLOUR

by

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The purity or grade of flour and the efficiency with which the milling operations have been performed is reflected in the content of bran powder and other substances originating from the outer layers of the grain.

The mineral matter content of wheat skins is about twenty to thirty times that of pure endosperm, so that the ash content of flour containing no extraneous mineral matter is an index of its bran powder content. The ash test is considered to be an accurate determination though according to SWANSON[1] differences of 0.02% or less are not significant.

In the presence of extraneous mineral matter the ash content ceases to be an index of bran content or extraction rate. Existing regulation in this country require that flour be enriched by the addition of 0.25% of calcium carbonate (in the form of *creta praeparata*). Because complete uniformity of distribution of the added mineral matter can not be secured, the ash content of the enriched flour is liable to give erratic results.

It is possible to determine the *creta* content and allow for this but the decomposition of calcium carbonate at 600° C — at which temperature the incineration of flour for ash content determination is made — is liable to lead to misinterpretation of results.

The ash determination, as an index of extraction rate, has been partly replaced by the determination of colour emplying the KENT-JONES AND MARTIN colour grader[2]. This test requires the use of expensive apparatus and its sensitivity is below that expected in a routine ash determination.

Some of the control methods for the estimation of flour grade have been considered by BROOKE[3] who suggested an evaluation of the flour grade by determining the concentration of flavone pigments in the flour. SIMPSON[4] described a method for determination of "yellowness" based on the extraction of flour with acetone and the colorimetric measurement of the "flavone yellow" colour produced by the addition of ammonia to the acetone extract.

BAILEY[5] suggested a physico-chemical method for determining the grade of flour based on the conductivity of eluates of centrifuged flour-water suspensions. The results were found to be influenced by pH variations and minor changes in temperature during digestion of the suspension.

Other alternate tests include the determination of crude fibre or of thiamine.

None of the methods except the KENT-JONES AND MARTIN colour grades has been found suitable as a replacement for the conventional ash test.

This paper deals with a method of determining the electrolyte content of filtered flour suspensions. The determination is based on the fact that if a solution containing several salts is passed through a hydrogen ion exchange column, the effluent contains a quantity of acid equivalent to the original salt content. By titration of the liberated acid the electrolyte content of the test solution can be determined. The presence of unknown acids in the solution, in addition to the mineral salts must be allowed for. This requires a separate titration of the acid originally present with subsequent subtraction from the titre of the effluent from the exchange column.

This general procedure has been previously employed by the authors for the determination of total electrolyte content of sugar products[6].

EXPERIMENTAL

Material

30 samples of flour were obtained from seven mills. The flours tested were of four types: straight flour of 75 and 85% extraction rate respectively; white and high extraction flour (0-40 and 40-80% extraction rate respectively) obtained in a combined milling system.

The extraction rates were calculated on uncleaned wheat basis.

The flour was milled from one or a mixture of the following wheats: Canadian Manitoba Wheat No. 3; Hard Red Winter No. 1; Soft Red Winter No. 2; French Soft Wheat; Moroccan Mixed Wheat, Turkish Soft Wheat and local hard and soft wheat.

Preparation of the column

25 g of analytical reagent grade Amberlite JR-120 cation exchange resin (a high capacity resin of nuclear sulphonic acid type, having a total exchange capacity of 4.2 milliequivalents per gram) were introduced into a graduated 100 ml glass column fitted with a tap. The dimensions of the resin column were 14 mm × 250 mm. The resin was supported on and covered with a layer of glass wool.

The resin was regenerated with 100 ml of a 10% hydrochloric acid solution and washed with distilled water until 50 ml of effluent required less than 0.05 ml of $0.1N$ sodium hydroxide for neutralization in the presence of phenolphthalein (2 drops of a 1 percent ethyl alcoholic solution).

The regenerating acid solution and distilled water were placed in a separatory funnel above the column and passed at rates of 6-8 and 10-12 ml per minute respectively.

Procedure

25 g of flour were suspended in 250 ml of distilled water (at 25° C) in a ground stoppered Erlenmeyer flask of 500-750 ml capacity. The contents were shaken vigorously during the preparation of the suspension and additionally three times at 10 minute intervals. At the end of 30 minutes, during which the flour suspension was kept at 25° C (± 2° C), the contents were filtered through a folded filter paper (Schleicher and Schüll No. 248, 12.5 cm diameter was used in our determinations). The first few turbid millilitres of filtrate were returned to the filter. At the end of 30 minutes, 50 ml of the almost clear solution were transfered to a 500 ml beaker, diluted to about 400 ml and after addition of 1 ml of phenolphtalein (1% alcohol solution) titrated with $0.1N$ sodium hydroxide from a semimicroburette, until the appearance of a permanent pale pink colour. Another 50 ml portion of the solution was passed — after dilution to about 100 ml — through the prepared column at a rate of 2 ml per minute. The column was washed until acid free with 400 ml of distilled water at a rate of passage of 6-8 ml per minute. After addition of phenolphtalein, the effluent was titrated as previously. The number of ml of normal base required to neutralize the acid liberated by water soluble electrolyte present in 100 g of flour, was compared with the ash content (gram in 100 g flour) of the tested samples.

Both figures were recalculated on a dry matter basis.

The ash content was determined by incineration at a temperature of 600° C, in a thermostatically controlled muffle furnace, the flour samples being placed in silica dishes.

The moisture content was determined by drying at 130° C for 1 hour in a ventilated semi-automatic (Brabender) oven.

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Results

The graphical presentation of results is given in Fig. 1.

A high factor of correlation — 0.90 — with the standard ash determination was found.

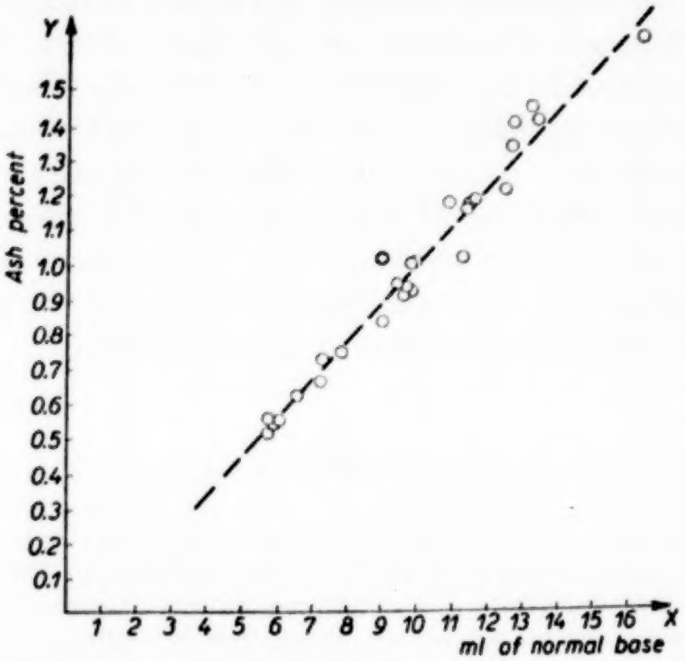

Fig. 1

The following simple formula based on the linear relationship between the ash and water soluble electrolyte determination, exists:

$y = 0.113\,x - 0.122$

where y = percentage ash

x = ml of normal base required for neutralization of acid liberated by water soluble electrolyte present in 100 g flour.

Both figures calculated on dry flour basis.

Duplicate determinations agreed to within 0.05 ml of normal base. The results were unaffected by storage under normal conditions.

The addition of calcium carbonate was found to have no influence on the titration value (see Table I). Acid consumed in the neutralization of calcium carbonate is liberated in equivalent amount during subsequent interaction of the soluble calcium salt with the column.

The given equation could not be used for testing pure bran.

As the quantity of acid required for complete column regeneration is relatively large and the time needed for complete acid removal rather long, tests have been made to employ the prepared column for several determinations without intermittent regeneration. 4 tests could be made by this procedure; results agreed within the limits of experimental error given previously.

Remarks

The proposed method for evaluation of the rate of extraction is influenced by changes in temperature of digestion, especially in high extraction flours.

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TABLE I

TITRATION VALUE (ml of 0.1N sodium hydroxide) AT VARIOUS LEVELS OF CALCIUM CARBONATE

No.	*Calcium carbonate addition (mg)*	*Titration value*
1	—	3.05
	40	3.02
	91	3.00
2	—	4.08
	105	4.15
3	—	3.92
	205	3.85
4	—	5.10
	123	5.02
	160	4.97
	172	5.02
	180	5.10

(All additions were made to 25 g of suspended flour).

It is assumed that even a higher factor of correlation could be obtained on testing flour samples of uniform granularity in a mill employing the same wheat.

This method, readily applicable to routine analysis, enables one to determine the "original" ash in the presence of added calcium carbonate.

Where estimation of the level of addition of *creta praeparata* in flour is needed, FEIGL's spot test[7] for testing fixed alkali has been found applicable.

The test is based on the fact that compounds furnishing hydroxyl ions react with a solution containing Mn^{+2} and Ag^{+} ions, a black or gray adsorption complex of metallic silver and manganese dioxide being formed.

$$4\ OH^- + 2\ Ag^+ + Mn^{+2} \rightarrow 2\ Ag + MnO_2 + 2\ H_2O$$

To test the flour for calcium carbonate content, 0.1 g of the flour is placed in the centre of a round shallow white porcelain crucible and incinerated until the ash becomes as white as possible. (In order to secure a quantitative conversion to calcium oxide an incineration in an electrically heated muffle furnace at a temperature of ap. 1100° C is required.)

After cooling, the ash is spotted with a drop of the reagent solution (containing 2.8 g $Mn(NO_3)_2$ and 3.39 g $AgNO_3$ dissolved in 100 ml water, treated dropwise with 0.1N NaOH to the point of precipitation and using the filtered solution).

The ash turns gray-black; the time of appearance of the spot as well as the intensity of colour depend on the calcium carbonate content. No spot was obtained on testing samples containing no added calcium carbonate.

The intensity of the black or gray spot can be compared with standards prepared by the same procedure. Differences of 0.1% calcium carbonate added in the range between 0.1-0.5% of added calcium carbonate may be detected.

SUMMARY

A method for the determination of flour grade is presented, employing a cation exchange column. Good correlation was found between the proposed method and the conventional ash determination. An equation has been established by which the ash of flour can be calculated with sufficient accuracy for practical purposes. The method enables the determination of "original" ash in the presence of added mineral matter. The estimation of the level of added calcium carbonate by a modified spot test procedure is described.

References p. 334

RÉSUMÉ

Une méthode d'analyse de farine est proposée, utilisant une colonne d'échangeur de cations. Les résultats obtenus par cette méthode correspondent tout à fait à ceux obtenus par la méthode habituelle de dosage des cendres. Une équation a été établie au moyen de laquelle la teneur en cendres des farines peut être calculée avec une précision suffisante pour la pratique. La méthode permet le dosage des cendres „originales" en présence de composés minéraux additionnés. L'estimation du taux de carbonate de calcium ajouté, par un procédé modifié d'analyse à la touche, est décrite.

ZUSAMMENFASSUNG

Eine Methode zur Analyse von Mehl wird beschrieben, welche eine Kationenaustauscher-Säule verwendet. Die mit dieser Methode erhaltenen Resultate stimmen gut mit denjenigen der üblichen Aschenbestimmungsmethode überein. Eine Gleichung wird aufgestellt, mit deren Hilfe der Aschengehalt des Mehls mit einer für die Praxis genügenden Genauigkeit berechnet werden kann. Die Methode erlaubt die Bestimmung der „ursprünglichen" Asche neben zugefügtem anorganischen Material. Die Menge des zugefügten Calciumcarbonates kann mit Hilfe einer Tüpfelmethode gefunden werden.

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THE DETERMINATION OF OXYGEN IN TITANIUM

VACUUM FUSION WITH A PLATINUM BATH

by

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The vacuum fusion method of analysis is generally considered the most satisfactory method of analysis for the determination of oxygen in high purity titanium. The method is based on the decomposition of the oxide in the presence of carbon and subsequent analysis of the evolved gases in a calibrated volume.

Two distinct techniques have been developed as a reaction medium in the furnace crucible: the iron bath method in which the sample is introduced into a graphite crucible containing molten iron and the "dry bath" method in which the sample is wrapped in tin and introduced into a graphite crucible containing graphite chips or coarse powder.

The use of the iron bath for refractory metals is accompanied by a tendency for the bath to solidify after a few samples have been analysed. This is probably due to the formation of "kish" graphite and high melting intermetallic compounds which float on the surface of the bath.

Both the iron bath and the dry bath methods are limited to the analysis of four to five samples per crucible. With a large number of titanium samples the shut down time for assembling a new furnace section and out gassing increased the analysis time per sample to a nearly prohibitive level. This work was initiated in an attempt to replace the iron bath with a metal which would eliminate the solidification of the bath when the operating temperature was held at 1800° C for an extended period of time. Platinum was selected as a medium for the reaction between the metal oxide and carbon because of its low volatility at the operating temperature and its inertness towards the gaseous reaction products.

Procedure

The apparatus which was used in this work has been adequately described[1].

The furnace is assembled with about twenty-five grams of platinum and the samples to be analysed in the loading tree. The crucible is outgassed at 2400° C (four to six hours) until the gas evolution rate is less than 0.1 micron-liters per minute. The temperature is dropped to 1400° C and the platinum added in four to five gram quantities over a period of ten minutes in order to pump off any residual gases in the platinum. The temperature is then raised to 1850° C and the bath outgassed until the blank is 0.2 to 0.3 micron-liters per minute. This usually takes about ten minutes after the furnace reaches 1850° C. The composition of the blank consistently ranges from 66-70% carbon monoxide, 5-10% nitrogen and the balance hydrogen.

A National Bureau of Standards iron sample is run to check the bath and this is followed by titanium samples until the bath reaches a composition of about 10% Ti. A NBS sample is run after the last sample to check the furnace for gettering. The furnace is then prepared for the next set of samples.

Pt Recovery

The amount of platinum evolved from the bath is negligible so that the recovery may be confined to the ingot obtained from the crucible. The ingot is pulverized in a diamond mortar and the platinum recovered chemically. The sponge obtained from the ignition of ammonium chloroplatinate is compressed into $^1/_2$" diameter by $^1/_4$" thick disks at 4000 p.s.i. The disks are melted into small ingots in a hydrogen flame with a oxy-hydrogen torch. These ingots are hammered into cubes, stamped and weighed. As an alternative the ingots from the crucible may be accumulated and refined commercially.

Discussion

The titanium which was used in this work was material prepared for a cooperative program for the analysis of oxygen in titanium. The results are given in Table I. Bath number one included four zirconium and three molydenum samples in addition to the eight titanium samples. Bath number two contained ten other titanium samples in addition to those given in Table I.

Platinum has been used in this laboratory for analysing molybdenum, tungsten, tantalum, chromium, zirconium, copper and high temperature alloys as well as titanium.

Conclusion

The use of platinum to replace the conventional iron bath for vacuum fusion analysis is economically feasible by virtue of the increased number of samples which can be run in one crucible.

The use of iron or tin cups to wrap samples is not necessary, thus eliminating an additional blank correction. The gas collecting time is shortened to fifteen minutes, thus lowering the blank correction to about 4 p.p.m. on a one gram sample. The need for running a series of iron standards with the samples has been eliminated. The bath has been held at 1850° C for thirty-six hours without any indication of solidification of the bath. The saving in time is such that the cost of the platinum is small in comparison to the man-hours saved. In this laboratory more samples have been analysed in two days than could be completed in three weeks using the iron bath.

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[1] R. S. McDonald, J. E. Fagel and E. W. Balis, *Anal. Chem.*, 27 (1955) 1632.

TABLE I

Bath No.	*Sample No.*	*$\%O_2$ (iron bath)*	*$\%O_2$ (Pt bath)*	*%Ti in bath*	*Blank (M-liters/min)*
1	50	0.168			0.55
		0.164			0.34
			0.163	1	0.19
			0.169	3.8	0.26
			0.163	4.6	0.26
			0.161	5.5	0.26
			0.166	5.3	0.55
			$\bar{X}$ = 0.164	S = 0.003	
2	49	0.047			0.17
		0.060	0.038	3.1	0.30
			0.036	4.8	0.44
			0.032	6.3	0.34
			0.035	8.1	0.15
			0.035	9.6	0.26
			0.032	11.0	0.34
			0.030	1.5	0.26
			0.037	5.8	0.12
			0.032	6.5	0.26
					0.26
			$\bar{X}$ = 0.034	S = 0.003	
2	51	0.274			0.29
		0.267			0.34
			0.274	2.2	0.49
			0.275	3.6	0.15
			0.277	5.4	0.26
			0.272	7.0	0.22
			0.275	8.0	0.26
			0.275	10.1	0.26
			$\bar{X}$ = 0.275	S = 0.002	

SUMMARY

Oxygen can be determined in titanium accurately by vacuum fusion with a platinum bath. The platinum bath is preferred to an iron bath or dry bath since more samples can be analysed in a bath without interference from gettering and solidification of the bath. The blank from adding iron or tin with the sample is eliminated.

RÉSUMÉ

L'oxygène dans un titane peut être dosé avec précision par fusion au vide, dans un bain de platine. Ce bain de platine est préféré à celui de fer, ou au bain sec; un plus grand nombre d'échantillons peuvent ainsi être analysés avant que le bain s'altère ou se solidifie. L'essai à blanc, du fer ou de l'étain ajouté à l'échantillon, est supprimé.

ZUSAMMENFASSUNG

Durch Vakuumschmelze in einem Platinbad kann der Sauerstoffgehalt in Titan genau bestimmt werden. Das Platinbad ist einem Eisen- oder Trockenbade vorzuziehen, da mehr Proben analysiert werden können ohne dass das Bad fest wird; der Blanko-Versuch mit Eisen oder Zinn erübrigt sich.

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THE MOVEMENT OF INORGANIC CATIONS IN PAPER CHROMATOGRAPHY

by

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Some information on the role of chemical reaction in differential ionic movement has been published in recent years. The "chemically active" solvents used in these studies have included alcohols containing diphenylthiocarbazone[1,2], potassium cyanide[3], ethylene diamine tetra-acetic acid[4], benzoylacetone[5] and several organic acids[6]. A further report[7] showed that the movement of a metal ion can be dependent on the anion in the original solution where there is the possibility of the anion forming a co-ordination compound with the metal.

These investigations have not examined the movement of metallic ions when chemical interaction produces a cationic complex. The following project was therefore planned to study simple cationic complexes such as the ammines.

Since the nitrates of metals have little tendency to form auto-complexes, these compounds were used as the stock solutions and the developing solvents included a range of aliphatic alcohols containing different concentrations of ammonium hydroxide.

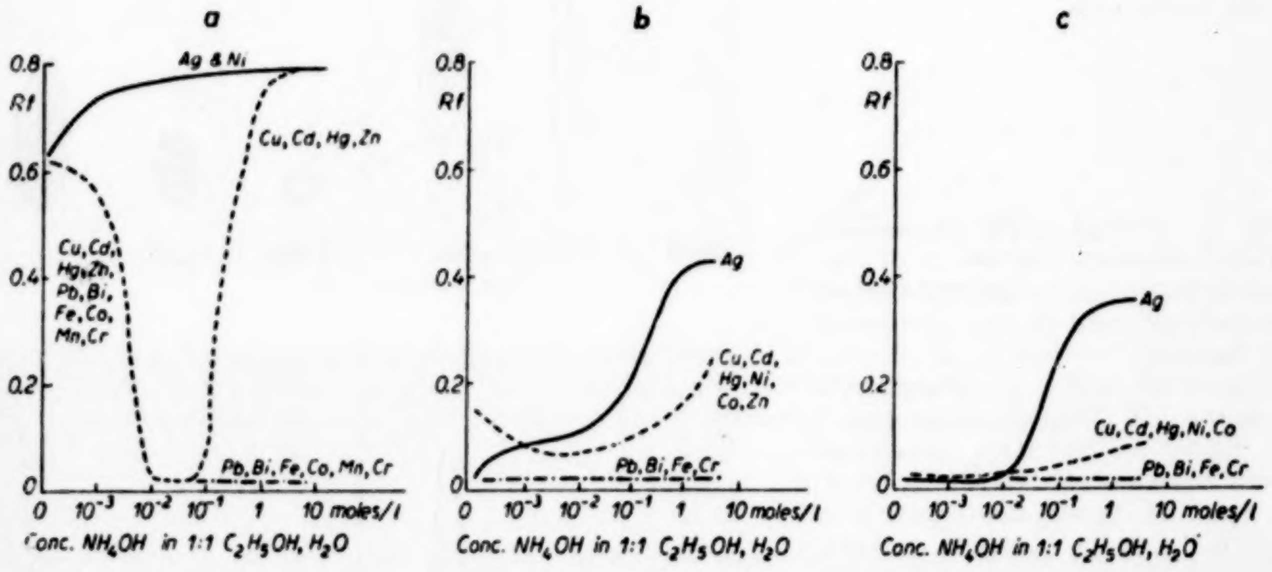

Fig. 1. The effect of ion concentration and solvent composition on apparent R_F values.

a. *M* nitrates of cations.

b. 0.1*M* nitrates of cations.

c. 0.01*M* nitrates of cations.

Procedure

Approximately 0.02 ml of either molar, deci-molar or centi-molar solutions of the nitrates of the cations Ag^+, Pb^{+2}, Bi^{+3}, Cu^{+2}, Cd^{+2}, Hg^{+2}, Fe^{+3}, Ni^{+2}, Co^{+2}, Mn^{+2}, Cr^{+3} and Zn^{+2} were "spotted" in similar positions on a series of rectangular paper strips prepared from Whatman No. 1 filter paper.

These papers were suspended in enclosed glass vessels with the lower end dipping into the solvent. One series of chromatograms was developed using solvents composed of 50% ethyl alcohol and 50% aqueous ammonium hydroxide solution, the concentration of the NH_4OH being varied between $10^{-3}M$ and $5M$.

Another series was developed using aqueous $2M$ NH_4OH, $2M$ NH_4OH in CH_3OH, $2M$ NH_4OH in C_2H_5OH and butyl or amyl alcohol saturated with $2M$ NH_4OH as solvents.

Finally, the movements of $0.1M$ solutions of the simple ions and complex ammines of Ag, Cu, Cd, Hg, Ni, Co and Zn were studied by developing spots of the ions with 100% water, methyl, ethyl, butyl or amyl alcohols.

After a standard period of development the papers were removed and the cations located by exposure to H_2S or treatment with other suitable reagent.

The apparent R_F value of the spot and any relevant increase in area during development was noted.

It was not considered practical to tabulate all the hundreds of results in this publication hence typical results for a series of elements have been shown in the accompanying graphs. The indicated R_F values may therefore not strictly apply to all the ions grouped together and individual R_F values can be supplied on request.

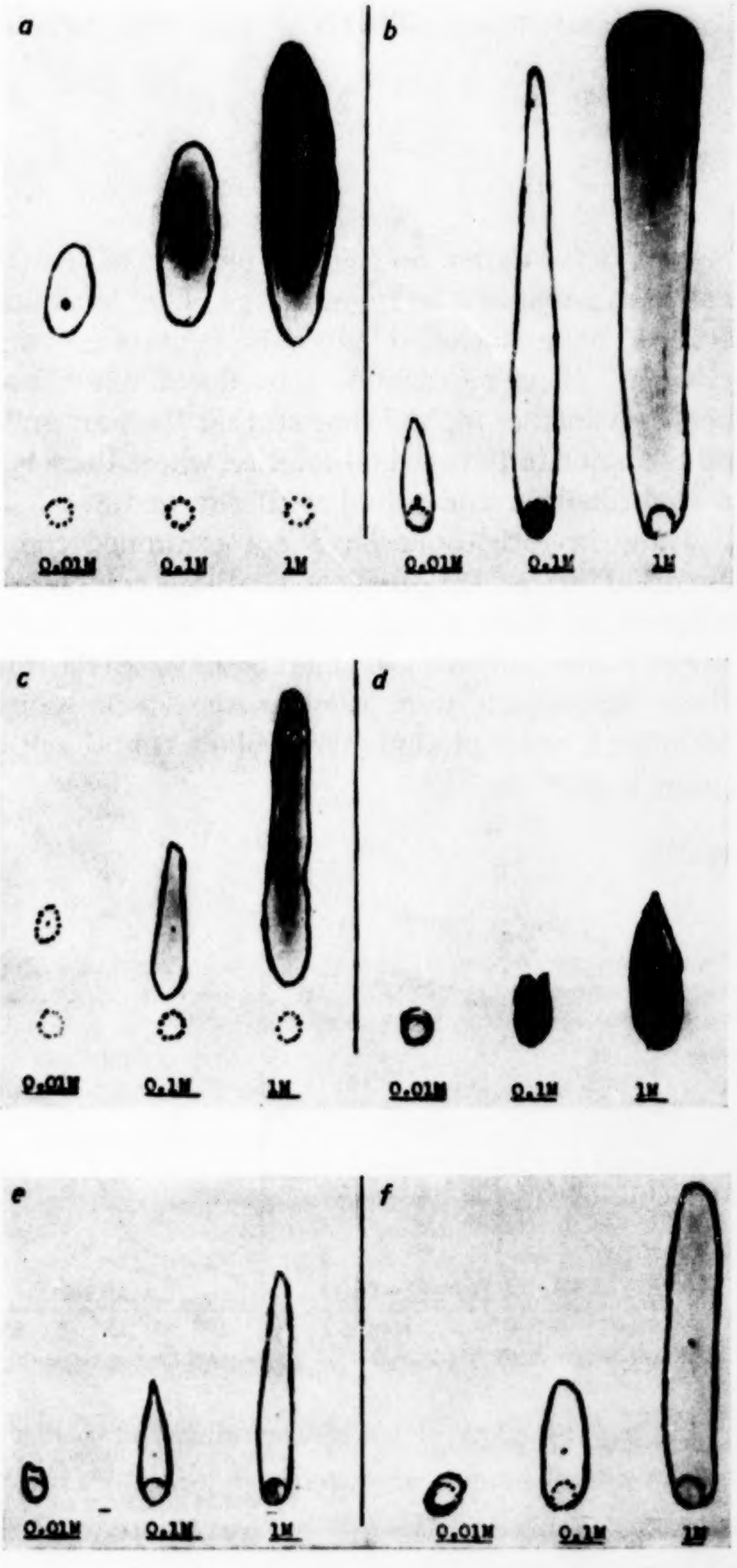

Fig. 2. Typical paper chromatograms showing the effect of the concentration of the spotted ion and the solvent used on the movement of the ion.
a. Spots of $AgNO_3$ developed with aqueous $2N$ NH_4OH solvent.
b. Spots of $Hg(NO_3)_2$ developed with aqueous $2N$ NH_4OH solvent.
c. Spots of $AgNO_3$ developed with $2N$ NH_4OH in C_2H_5OH solvent.
d. Spots of $Cu(NO_3)_2$ developed with $2N$ NH_4OH in C_2H_5OH solvent.
e. Spots of $Cd(NO_3)_2$ developed with $2N$ NH_4OH in CH_3OH solvent.
f. Spots of $Ni(NO_3)_2$ developed with $2N$ NH_4OH in CH_3OH solvent.

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RESULTS

The effect of variations in the concentration of the "spotted" ion and the concentration of ammonium hydroxide in the solvent on the R_F value is shown by the graphs (Fig. 1) and typical chromatograms (Fig. 2).

With molar solutions of the cations, using a pure solvent, the simple ions moved upwards with the aqueous front but there was marked tailing back to the original spot. In the presence of NH_4OH, Ag and Ni ions were apparently rapidly converted to the ammine complex with a resultant increase in R_F. The other elements initially ceased to move (formation of insoluble hydroxide) and Cu, Cd, Hg and Zn only gave increased R_F values in the presence of high concentrations of NH_4OH. Due to the long tailing effect and diffusion of the ions, the area occupied by the upper concentration of ions was approximately four times larger than the area of the original spot and the area of tailing, eight to ten times the area of the original spot.

With deci-molar and centi-molar solutions of the cations, the only movement observed was upward tailing from a high concentration of ion at the original spot. The one exception was Ag^+ ion in the presence of 2 or $5M$ NH_4OH which moved away from the origin giving an oval spot.

The size of the tail with $0.1M$ solute was approximately five times the area of the original spot while $0.01M$ solutes gave tails nearly equal in area to the spot.

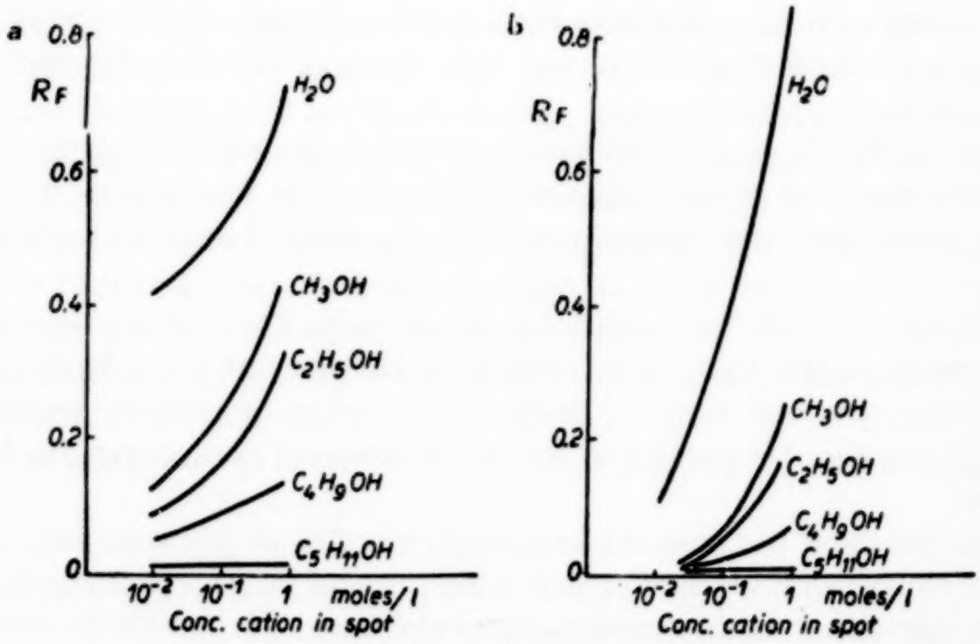

Fig. 3. The effect of carrier solvent and concentration of solute on movement of cations.
a. Silver nitrate (all solvents saturated with $2N$ NH_4OH).
b. Nitrates of Cd, Ni, Zn (all solvents saturated with $2N$ NH_4OH).

The influence of the concentration of solute and the nature of the carrier solvent on the R_F values in the presence of similar amounts of NH_4OH is shown in Fig. 3.

With the exception of molar solutes in the aqueous solvent, observed movements were due to tailing or diffusion from the original spot. Of the elements not shown in Fig. 3, Pb, Bi, Fe, Mn and Cr did not move from the original point of application under any conditions. Cu, Hg and Co showed appreciable movement and tailing in aqueous solution but gave R_F values of the order of 0.05 with the lower alcohols and showed no movement in amyl alcohol.

In the series which compared the movement of simple ions and the ammine complex ions in various solvents, movement was found to be restricted to slight tailing from the original spot. The simple ions tailed sufficiently to give R_F values of the order of 0.05 in water, 0.09 in methanol, 0.02 in butanol and no movement was observed in amyl alcohol. The ammine complexes, formed by adding an excess of NH_4OH to the nitrate solution, showed reduced tendencies for movement. Tailing occurred only with Ag, Cd, Ni and Co complexes using water and the lower alcohols as solvents.

DISCUSSION

From earlier studies[3,4] it was concluded that the movement of cations and the area of the developed spot were directly related to the relative concentration of cation spotted on the paper and the concentration of active agent in the solvent.

The work of MARTIN[7] has indicated that similar arguments might apply in the case of halide compounds of many elements.

In these examples, the cations reacted to form either non-polar compounds or anionic complexes. Under these conditions, the predicted negative charge of the paper would not tend to attract or adsorb the ions to any marked degree.

However, using cationic complexes such as the ammines, the factor of adsorption was considered of major importance and the results of the investigation have confirmed this view.

Using KCN or EDTA as the active components in the solvent, marked changes in R_F value were observed when sufficient "active" agent was present to completely convert the solute into the anionic complex. No such change was observed using NH_4OH.

The formation of insoluble hydroxides of the metals would explain the absence of any movement of the ions under certain conditions but it far from satisfies the majority of the observed results. Probably the most important anomaly is the variation in R_F value of a particular ion when different concentrations are spotted on the paper.

These variations and the presence of excessive tailing of the solutions can only be satisfactorily explained if we predict that adsorption of positively charged ions by the paper is a major factor in the movement of the ions.

It can be assumed that a given brand of paper will possess a certain adsorbent capacity per unit area. If the amount of solute spotted on a small area of the paper exceeds the adsorbent capacity of that area, then it is reasonable to suggest that the excess can enter the moving solvent phase. As the solvent rises up the paper, some solute will be adsorbed by the fresh paper surface and give rise to the observed tails. (In the presence of free acid in the mobile phase, this effect may be minimized by the preferential adsorption of the hydroxonium ion by the paper.)

In the case of molar solutions, the amount of solute present was far greater than the adsorptive capacity of the paper hence the bulk of ions moved upwards with the aqueous wave front giving high R_F values. In the presence of NH_4OH, many of the cations form insoluble hydroxides and this would account for the zero R_F values shown on the graphs.

Apparently, deci-molar solutions just exceed the adsorptive capacity of the paper and excess ions tail upwards until sufficient area of paper has been covered to adsorb the excess of solute. The absence of movement with most centi-molar solutions may then be explained as being due to complete adsorption of this concentration of salt by the paper.

If the hypothesis is reasonable, it is interesting to note that the R_F value (and therefore area of paper covered by the tail) of the ammines (*i.e.* solvents containing $5M$ NH_4OH in Fig. 1) is greater than the R_F value (and area) of the corresponding amount of simple ion.

The absence of movement of the ammine complexes when they were spotted directly on the paper and developed by pure solvents can readily be explained by the relatively low stability of the complexes. The first passage of solvent would tend to remove any excess of NH_4OH present and the ammine complex would decompose to the insoluble hydroxide. LEDERER[8] has examined the movement of some ammine complexes of Co(III) but as the developing solvents were saturated with acid, the results were not considered relevant to this study.

Finally, the variations in R_F values shown in Fig. 3 which correspond to changes in the solvent liquor are in accordance with predicted behaviour. In this investigation, the mobile metal complexes are all polar in nature, hence will have the greatest solubility in highly polar solvents such as water and reduced solubility in the series of alcohols. If the compound formed between the cations and the "active" agent were non-polar, then it could be assumed that the order would have been reversed.

The investigation recorded is one of a series planned to make some contributions to an understanding of the factors which govern the movement of inorganic ions on filter paper. The effect of variations in the concentration of original solute on the movement of ions was first observed in preliminary electro-chromatography studies[9] and it is felt that this research has confirmed in many respects the important role adsorption may play in the movement of cations.

The only qualitative separation which appears feasible is the separation of small amounts of silver (which moves as a compact spot) from the other elements examined by using an ethanolic solvent $5M$ in respect to ammonium hydroxide.

CONCLUSIONS

The results of this study confirm earlier opinions that the movement and spot areas of paper chromatograms of metal ions will vary with many conditions if the metal is allowed to exist in an ionic form. With cations, a controlling factor is the adsorptive capacity of the paper and with complex anions containing the metal, the concentration of complexing agent in the solvent is of prime importance.

SUMMARY

The paper chromatographic behaviour of twelve metal ions has been examined using alcoholic solvents containing various concentrations of ammonium hydroxide. It was found that the movement of the ions was dependent not only on the amount of NH_4OH present and the alcohol used, but also on the concentration of ion spotted on the paper. It is suggested that adsorption of the ions by the paper is a major factor controlling the movement of ionic compounds or complexes.

RÉSUMÉ

On a fait l'examen chromatographique de douze ions métalliques en se servant de solvants alcooliques contenant des concentrations variées d'hydroxyde d'ammonium. On a trouvé que le mouvement des ions dépendait non seulement de la quantité de NH_4OH présente, et de l'alcool employé, mais aussi de la concentration de l'ion en tache sur le papier. Il nous semble que l'adsorption des ions par le papier est un facteur important dans le mouvement des composés ioniques et complexes.

ZUSAMMENFASSUNG

Alkoholische Lösungsmittel, die verschiedene Konzentrationen von Ammoniumhydroxid enthielten, wurden verwendet, um das chromatographische Verhalten von zwölf Metallionen zu verfolgen. Man konnte feststellen, dass die Ionenbewegung nicht nur von der Menge des vorhandenen NH_4OH und des verwendeten Alkohols abhängt, sondern auch von der Ionenkonzentration auf dem Papier. Wir müssen daher annehmen, dass die Papieradsorption von Ionen ein bestimmender Faktor der Bewegung von Ionen- und Komplexverbindungen ist.

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R.Rf. METHODS OF CHEMICAL ANALYSIS AND CHROMATOGRAPH ZONE LOCATION

A CIRCUIT COMBINING "FULL-WAVE RECTIFICATION" WITH "NEGATIVE ZERO SET-BACK"

by

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The circuit illustrated in Fig. 1 is especially suited for the purpose of obtaining increased sensitivity when using the author's R.Rf. method of chromatographic zone location[3,8,9] and also for his R.Rf. method of chemical analysis and titration[4]. By the employement of "full-wave rectification" the rectified current is (approximately) doubled, and by combining this with the "negative zero set-back" circuit[4] the sensitivity of the measuring instrument (either micro-ammeter or galvanometer) is increased. The negative zero set-back principle[4,7] was developed by the author from J. J. Dowling's original ultramicrometer[5,6].

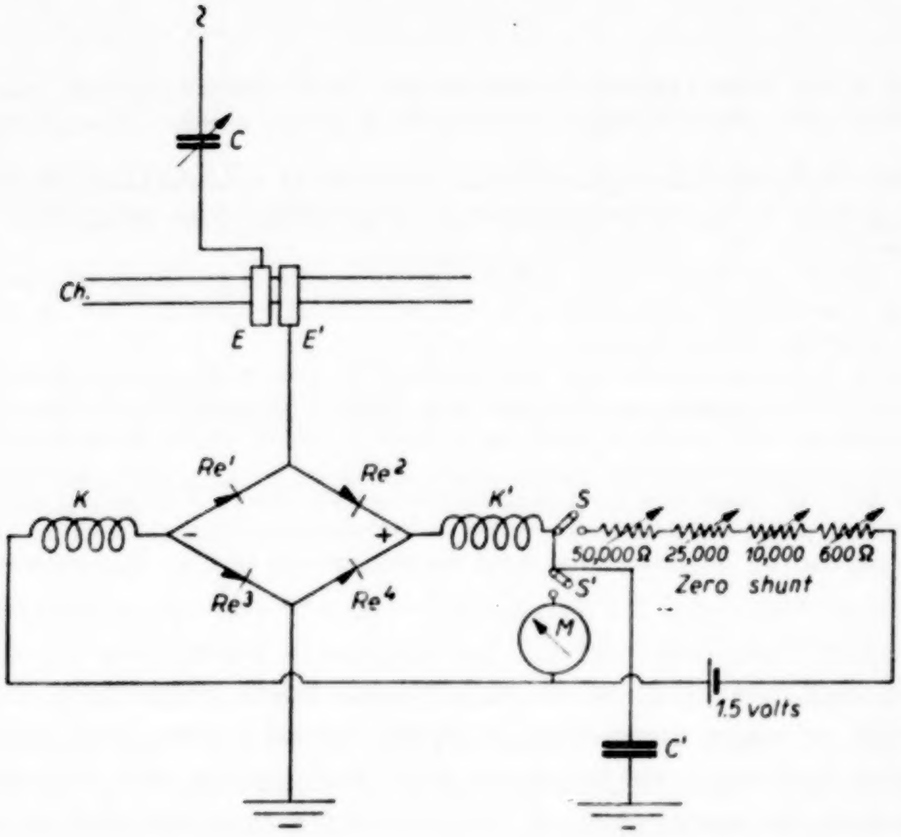

Fig. 1. This diagram illustrates the application of combined full-wave rectification and negative zero set-back to rectified radio-frequency zone location.

Fig. 2 illustrates the increased sensitivity obtained by two "negative zero set-backs" in succession[4].

In the titration C Fig. 2, although the solution was eight times more dilute than that graphed at A, C is the better of the two. Graph B shows the same concentration titrated without the application of negative zero set-back.

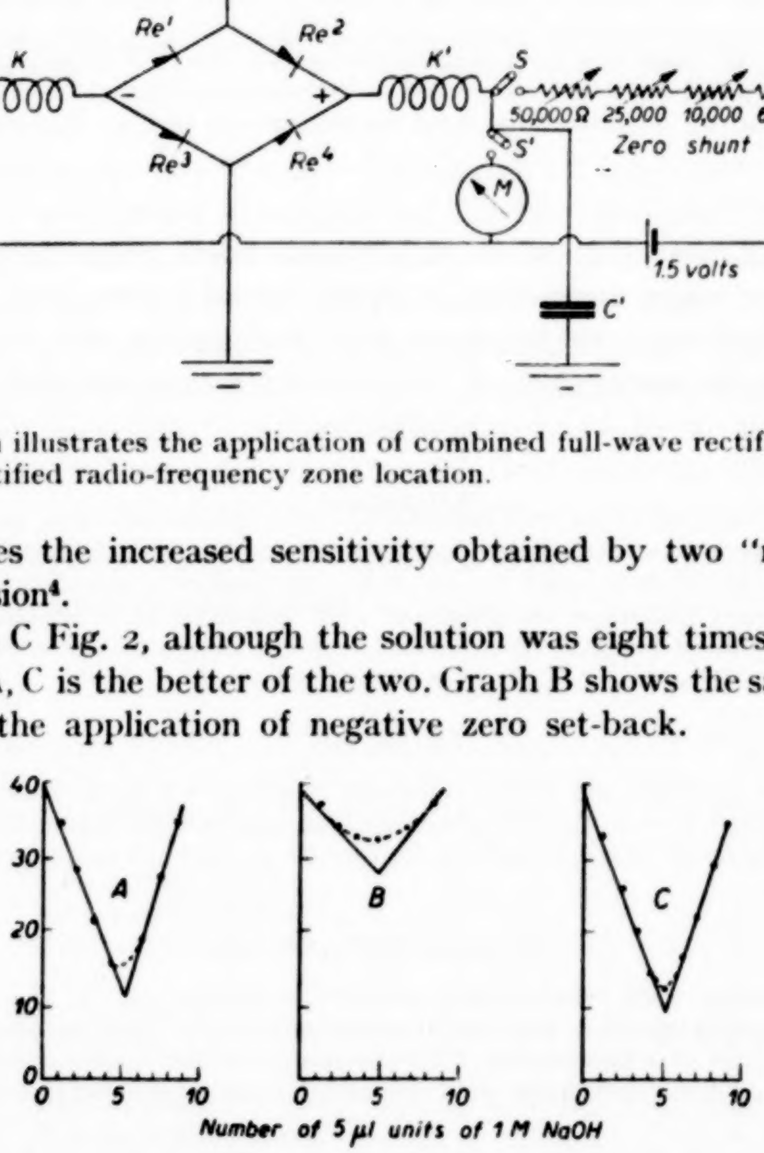

Fig. 2. Diluted HCl titrated by 1 M NaOH. A: 5 units in 5 ml; B: 5 units in 40 ml; C: 5 units in 40 ml. Graphs A and B are normal titrations and graph C is a titration of the same concentration as B after two "negative zero set-backs".

Full-wave rectification and negative zero set-back combined

Fig. 1 shows the new circuit as applied to chromatography.

E and E′ are the electrodes of a R.Rf. chromatograph localizer[3,8,9]. Radio-frequency currents are fed to E from a Rf. oscillator and are regulated by four rheostats in series with a 1.5 volt battery. This method of series regulation ensures a minimum drain on the battery. The battery circuit is switched at S. A second switch S′ enables the microammeter to be disconnected.

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Procedure

The electrodes of the Zone Localizer[8,9] are bridged by a chromatograph zone as indicated.

1. With switch S open, the coupling C is adjusted to give a nearly full scale meter deflection, say 90 μ amps.

2. Keeping the instrument settings constant the zone is now removed from the electrodes and replaced by a part of the chromatograph on which there is no zone. This bare paper will cause a small deflection "X" microamps.

3. Switches S and S′ are now closed and the meter needle is put back to zero by adjustment of the zero shunt. The coupling meanwhile is not altered. The amount "X" in micro-amps must be added to all readings which follow.

4. If the zone or spot has insufficient conductivity to give a 90 μ amps reading the coupling must be increased until the meter again reads 90 μ amps. This will give the bare paper a reading of X′. Having returned the needle to zero once more X + X′ must be added to all succeeding meter readings.

This negative zero set-back can be repeated five or six times if required and each time the coupling is increased the field at the electrodes is increased so that the calibration of the meter is extended far beyond its normal range, and measurements of high impedance substances are now obtainable.

It is anticipated that this work will be extended eventually to include the chromatography of plant pigments, proteins, blood serum and other branches of chromatography and may be required even to measure the impedance of non-conductive zones. In some cases it may be necessary to add either a stage or stages of transistor or of valve amplification.

SUMMARY

This paper describes a new circuit especially applicable to Blake's R.Rf. impedance method of chromatograph zone location, and for his R.Rf. method of conductimetric analysis.

The circuit combines full-wave rectification with negative zero set-back. The Rf. field at the electrodes of the zone localizer is increased and the range of the measuring instrument is extended.

RÉSUMÉ

L'auteur décrit un nouveau circuit spécialement applicable à sa méthode de localisation des zones en chromatographie et à sa méthode d'analyse conductimétrique, toutes deux à courant de radiofréquence redressé. Par un artifice, ce circuit permet d'augmenter le domaine de l'instrument de mesure.

ZUSAMMENFASSUNG

Ein neuer Stromkreis wird beschrieben, welcher insbesondere für die Zonenlokalisierungsmethode in der Chromatographie und die konduktometrische Analysenmethode des Verfassers (zwei Methoden, welche gleichgerichtete Radiofrequenz-Ströme verwenden) geeignet ist. Durch einen Kunstgriff in diesem Stromkreis wird der Bereich des Messinstruments erweitert.

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SPEKTROPHOTOMETRISCHE UNTERSUCHUNGEN EINIGER ANALYTISCH WICHTIGER KOMPLEXE DES TITANS IN LÖSUNG

von

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Bei den Reaktionen des vierwertigen Titans mit *o*-Diphenolen und Polyphenolen entstehen gelbe bis orangerote Lösungen der Chelate mit einer stark polaren Ti-O Bindung und einem beständigen fünfgliedrigen Ring in schwach saurem Milieu (pD = 5.5-5.6). Bei den Reaktionen mit *o*-Phenolcarbonsäuren ist die Empfindlichkeit kleiner (pD = 4.6-4.9). Eine hohe Empfindlichkeit ergeben *peri*-Diphenole. Die Reaktion der Chromotropsäure gehört zu den analytisch wichtigsten und empfindlichsten Reaktionen des Titans (pD = 5.9)[1].

Die Beständigkeit des entstehenden Chelates und auch die Empfindlichkeit der Ti-Reaktion nimmt mit der sinkenden Stabilität der intramolekularen Wasserstoffbindung des betreffenden Phenols ab. Eine sehr stabile Wasserstoffbindung wurde bei der Chromotropsäure nachgewiesen[2].

TABELLE I

DIE EMPFINDLICHKEIT DER TÜPFELREAKTIONEN MIT Ti^{+4} BEI pH 4-6

Reagens	*pD*
Chromotropsäure	5.9
1.8-Dioxynaphtalin	5.6
Dioxy-R-Säure	5.6
Tiron	5.5
Pyrokatechin	5.5
Guajakol	4.6
Vanillin	3.9
Vanillinsäure	3.9
Pyrokatechinaldehyd	5.6
Pyrogallolcarbonsäure	5.6
Gallussäure	5.6
Pyrogallol	5.5
Salicylsäure	4.9
p-Aminosalicylsäure	4.9
m-Kresotinsäure	4.6
β-Resorcylsäure	4.9
Sulfosalicylsäure	4.9

Bei Methyläthern der *o*-Diphenole ist die Reaktion mit Ti^{+4} abgeschwächt (Guajakol, Vanillin), Dimethyläther reagieren überhaupt nicht (Veratrol). Ebenso findet bei den Derivaten der Salicylsäure mit substituierten Phenolhydroxyl- oder Carboxylproton

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(Acetosalicylsäure, Methyläther der Salicylsäure) keine Reaktion statt. Die Substitution durch weitere –OH oder –COOH Gruppen bei Diphenolen und durch –OH, $-NH_2$, $-SO_3H$ Gruppen bei Phenolcarbonsäuren ist praktisch ohne Einfluss auf die Empfindlichkeit der Reaktionen.

Beim Konzentrieren und Verdampfen der Lösungen von farbigen Ti-Komplexen der Chromotropsäure, des 1.8-Dioxynaphtalins, Pyrokatechins, Tirons oder der Sulfosalicylsäure findet eine Zersetzung statt und es entstehen nur Gemische von hydrolytischen Produkten uneinheitlicher Zusammensetzung. Nur aus amoniakalischen Lösungen des Pyrokatechins und Ti^{+4} gelang es ROSENHEIM[3] krystallinische Pyrokatechinatkomplexe $Me_2TiR_3.xH_2O$ zu isolieren. Aus neutralen Lösungen der Salicylsäure und Ti^{+4} wurden unter besonderen Bedingungen Halogenotitantrisalicylsäuren[4] und deren hydrolytische Produkte[5] sowie einige, den Pyrokatechinatkomplexen ähnliche, Verbindungen[3] isoliert.

Das Isolieren eines Chelats schliesst die Möglichkeit der Existenz einer grösseren Anzahl von Komplexverbindungen in der Lösung nicht aus und kann einen groben Eingriff in die komplizierten Gleichgewichtszustände der Komplexe bedeuten, sodass das Endprodukt nicht immer den Komplexen in der Lösung entspricht. Einen besseren Einblick in die Verhältnisse in der Lösung bieten spektrophotometrische Methoden, unter denen die Methode der kontinuierlichen Variationen[6] in äquimolaren und nicht-äquimolaren Lösungen, die logarithmische Analyse[7], die Methode der molaren Verhältnisse[8] und die graphische Analyse der pH-Kurven, die wir in unserer Arbeit verwendet haben. Dadurch konnten wir in den Lösungen von Ti-Chelaten mit Chromotropsäure, Pyrokatechin, Tiron, Sulfosalicylsäure, Gallussäure und Pyrogallolcarbonsäure eine stufenweise Entstehung von Komplexen in Abhängigkeit vom pH, von der absoluten und relativen Konzentration der Komponenten und der Zusammensetzung der Lösung nachweisen. Bei komplizierten Gleichgewichtszuständen zwischen den normalen Komplexen, Hydroxokomplexen und Acetatokomplexen in den gepufferten Lösungen, stiessen wir jedoch bei einigen wenig stabilen Komplexen auf Schwierigkeiten, die bei den Schlussfolgerungen berücksichtigt werden müssen. Das Verfolgen der Komplexe in der Lösung und die Feststellung der Entstehungsbedingungen eines einheitlichen und stabilen Komplexes ist von besonderer Bedeutung für die Aufstellung einer exakten Methode der photometrischen Titanbestimmung.

Es zeigte sich, dass in den Lösungen der Chromotropsäure mehrere färbige Ti-Verbindungen entstehen können[9]. In äquimolaren Lösungen der Komponenten bei pH 1.5-1.6 sind zwei dissoziierte Komplexe TiR und TiR_2 wahrnehmbar. Bei Chromotropsäureüberschuss bildet sich bei pH 1.9 nur ein Komplex TiR_2.

Im Gebiet von pH 2-3 bildet sich beim Überschuss der Chromotropsäure oder bei hohen absoluten Konzentrationen der Komponenten in äquimolaren Lösungen auch ein Komplex TiR_4. Erst im Gebiet von pH 3.32-4.69 ensteht ein einziger roter Komplex TiR_3 (λ_{max} 470 mμ), welcher bei pH 3.8-5.5 in einen stabilen orangefarbenen Hydroxokomplex $TiOHR_3$ (λ_{max} 420 mμ) übergeht.

Die Absorptionskurven der Komplexe in Abhängigkeit vom pH besitzen 2 isobestische Punkte (590 mμ und 467-470 mμ), die einen quantitativen Übergang zwischen drei Komplexen TiR_2, TiR_3, $TiOHR_3$ anzeigen. Der letzte Übergang ist mit einer grossen Verschiebung des Absorptionsmaximums von 472 mμ bei pH = 2 bis zu 420 mμ bei pH = 5.5 verbunden. Bei der Komplexbildung wird das zweite

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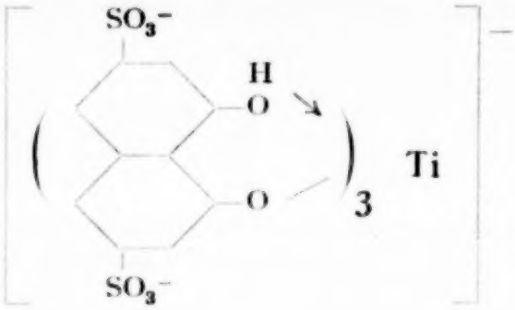
Hydroxylproton der Chromotropsäure quantitativ nicht abgespalten, was zur folgenden Formulierung von TiR_3 führen kann:



Die Bildung von höheren Hydroxokomplexen und gemischten Acetatokomplexen bei pH > 6 ist nicht ausgeschlossen[10].

Die Absorptionskurven von Ti-Komplexen mit 1.8-Dioxynaphtalin bei verschiedenen pH-Werten besitzen nur einen isobestischen Punkt bei 480 mμ (Verschiebung des Maximums von 495 mμ bei pH 2.74 bis 435 mμ bei pH 5.08). Die entstehenden Komplexe sind weniger stabil, man kann jedoch einen ähnlichen Reaktionsmechanismus wie bei der Chromotropsäure voraussetzen.

In äquimolaren orangen Lösungen des Tirons und Pyrokatechins ensteht bei pH 3-4 ein Gemisch von Komplexen TiR und TiR_2, das bei pH 5.1-5.4 in einen gelben Komplex TiR_3 übergeht.

Beim Überschuss des Komplexbilders entsteht der Komplex TiR schon bei pH 1.5. Der Komplex TiR_2 geht von pH 2.6 quantitativ in TiR_3 über (isobestischer Punkt an den Absorptionskurven bei 450-455 mμ). Ein relativ stabiler Komplex bildet sich im Gebiet von pH 4.0-6.0. Beide Protonen des Komplexbildners werden schon in der ersten Phase der Reaktion abgespalten[11].

In den gelben Lösungen der Sulfosalicylsäure mit Ti^{+4} wurde nach der Methode der kontinuierlichen Variationen bei Überschuss der organischen Komponente und auch durch Analyse der pH-Kurven der relativ wenig stabile Komplex TiR_2 ($\lambda_{max} = 355$ mμ) im Gebiet von pH 2.0-4.8 identifiziert. In sauren Lösungen kann man auch die Existenz des komplexen Ions TiR^+ bei pH < 1.8 voraussetzen[12].

Titankomplexe der Gallussäure und Pyrogallolcarbonsäure

Die spektrophotometrischen Untersuchungen wurden nun auf die Titankomplexe der Gallussäure und Pyrogallolcarbonsäure erweitert, deren Konstitution bis heute noch nicht bekannt ist.

Reagenzien

Die organischen Reagenzien wurden sorgfältig auf Reinheit geprüft, eventuell durch Umkrystallisieren gereinigt.

Die Titanlösungen wurden durch Auflösen von $TiCl_4$ in einer kleinen Menge siedender konzentrierter Schwefelsäure bereitet und nach entsprechender Verdünnung gravimetrisch eingestellt. Die pH-Werte der Lösungen wurden mit verdünnter Schwefelsäure, 0.1 *N* und *N* Natriumacetat, 0.5 *M* und 0.4 *M* Kaliumbiphtalat und *N* NaOH eingestellt und elektrometrisch genau kontrolliert.

Die Absorptionskurven wurden mit einem Beckman Quarzspektrophotometer Model DU aufgenommen, qualitative Anwendungen der Methoden mit dem Pulfrich Photometer verfolgt.

Titankomplexe der Gallussäure

Die Absorptionskurven von orangegelben Lösungen der Gallussäure mit Ti^{+4} weisen bei pH 2.31 bei Anwesenheit von überschüssiger Gallussäure ein zerstreutes Maximum 375-390 mμ auf. Mit wachsenden pH-Werten verschiebt sich das Absorptionsmaximum bis zu 365 mμ und von pH 3.23 an bleibt es weiterhin konstant. Die Kurven durchlaufen einen wenig ausgeprägten isobestischen Punkt bei 435 mμ im Gebiet von pH 2.5-3.5 (Fig. 1).

Die pH-Kurven bei einem Überschuss an Gallussäure sind für 430-500 mμ den pH-Kurven der Pyrokatechin- und Tironkomplexe mit Ti^{+4} sehr ähnlich. Bei pH = 1.5-2.3 bemerkt man einen

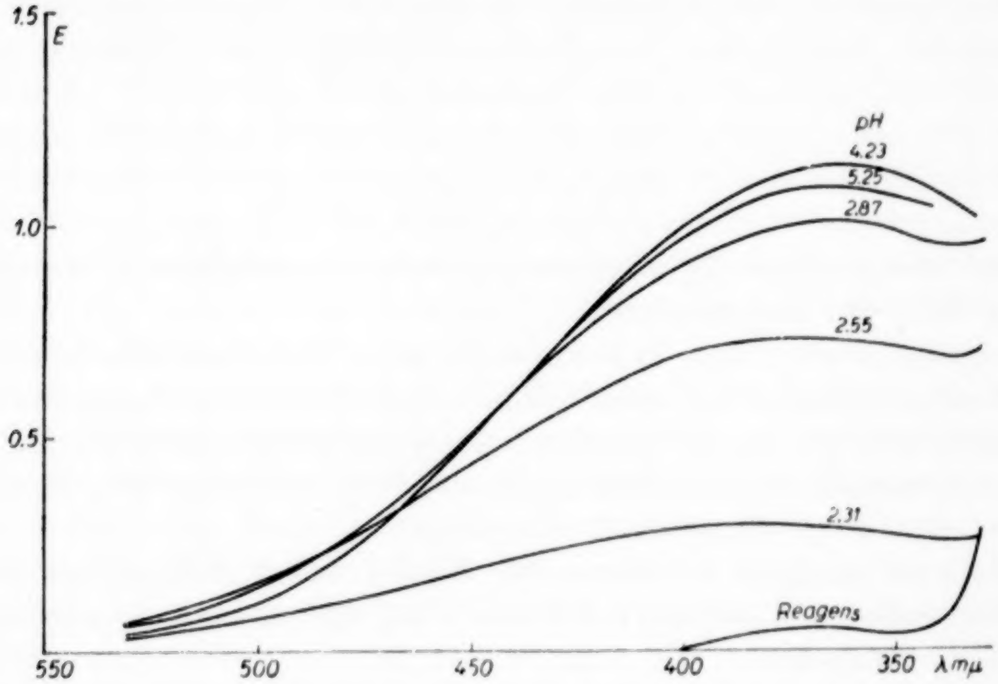


Fig. 1. Absorptionskurven der Komplexe der Gallussäure mit Ti^{+4} bei verschiedenem pH (Acetatpuffer).
$c_{Ti} = 6.363 \cdot 10^{-5} M$, 10 ml 1% Lösung der Gallussäure auf 50 ml.

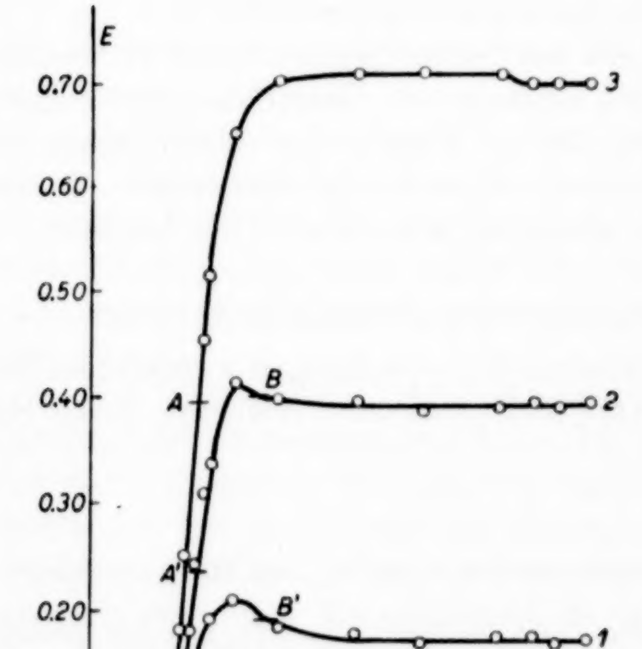


Fig. 2. pH-Kurven der Gallussäurekomplexe mit Ti^{+4}.
$c_{Ti} = 6.363 \cdot 10^{-5} M$, 20 ml 1% Gallussäurelösung auf 50 ml.
Ionenstärke $\mu = 0.04$. Kurve 1: 500 mμ; 2: 470 mμ; 3: 430 mμ (Acetatpuffer).

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scharfen Aufstieg der Extinktion, bei pH 2.4 ein Maximum und im Gebiet von pH 2.4-3.5 wieder ein Absinken der Kurven bei 470 und 500 mμ. Die Kurve für 430 mμ erreicht kein Maximum, die Extinktion bleibt von pH 3.3-5.8 konstant (Fig. 2).

Durch die logarithmische Analyse des steigenden Zweiges der pH-Kurven bei pH 1.61-2.36 bezogen auf

$$\log \frac{\mathrm{TiR}_n}{\mathrm{Ti}} = \log \frac{E}{E_0\text{-}E} = n\mathrm{pH} + \mathrm{K}_1$$

wo E_0 eine konstante Extinktion im wagrechten Aste der pH-Kurve ausdrückt (Fig. 3), wurde die Anzahl der abgespaltenen Protonen gefunden.

λ mμ	*n*
500	2.74
470	2.82
430	3.27

Für einen niedrigeren pH-Wert ist die Tangente der Kurve kleiner, 2.0-2.14.

Wenn man die Dissoziation der Gallussäure in die erste Stufe ($\mathrm{pK}_1 = 4.4$) und eine gleichzeitige Abspaltung von 2 Protonen der phenolischen Hydroxyle bei der Komplexbildung voraussetzt,

$$\mathrm{Ti}^{+4} + \mathrm{RH}_2^- \rightleftarrows \mathrm{TiR} + 2\mathrm{H}^+$$

entsteht bei pH 1.7-1.8 auch bei einem Überschuss des Komplexbildners überwiegend der Komplex TiR, der mit wachsenden pH-Werten in ein Gemisch von Komplexen TiR und TiR_2 übergeht. Bei pH 2.4 ist die Bildung des Komplexes TiR_2 quantitativ, der absinkende Teil der pH-Kurve indiziert sodann den quantitativen Übergang des Komplexes TiR_2 in TiR_3 der einheitlich bei pH 3.5-5.8 entsteht und durch einen isobestischen Punkt in den Absorptionskurven angedeutet wird.

Wenn der steigende Teil der pH-Kurve überwiegend den Gleichgewichtszustand

$$\mathrm{TiR} + \mathrm{RH}_2^- \rightleftarrows \mathrm{TiR}_2 + 2\mathrm{H}^+ \quad (\mathrm{K}_2)$$

darstellt und die sinkenden Äste der Kurven den Gleichgewichtszustand

$$\mathrm{TiR}_2 + \mathrm{RH}_2^- \rightleftarrows \mathrm{TiR}_3 + 2\mathrm{H}^+ \quad (\mathrm{K}_3)$$

ausdrücken, so ist für den Punkt A (Fig. 2):

$$[\mathrm{TiR}] = [\mathrm{TiR}_2]$$

und für den Punkt B:

$$[\mathrm{TiR}_2] = [\mathrm{TiR}_3]$$

Für die Teil-Bildungskonstanten der Komplexe können wir schreiben:

$$\log \mathrm{K}_2 = 2 \log[\mathrm{H}_{1\text{-}2}] - \log [\mathrm{RH}_2^-]$$

$$\log \mathrm{K}_3 = 2 \log[\mathrm{H}_{2\text{-}3}] - \log [\mathrm{RH}_2^-]$$

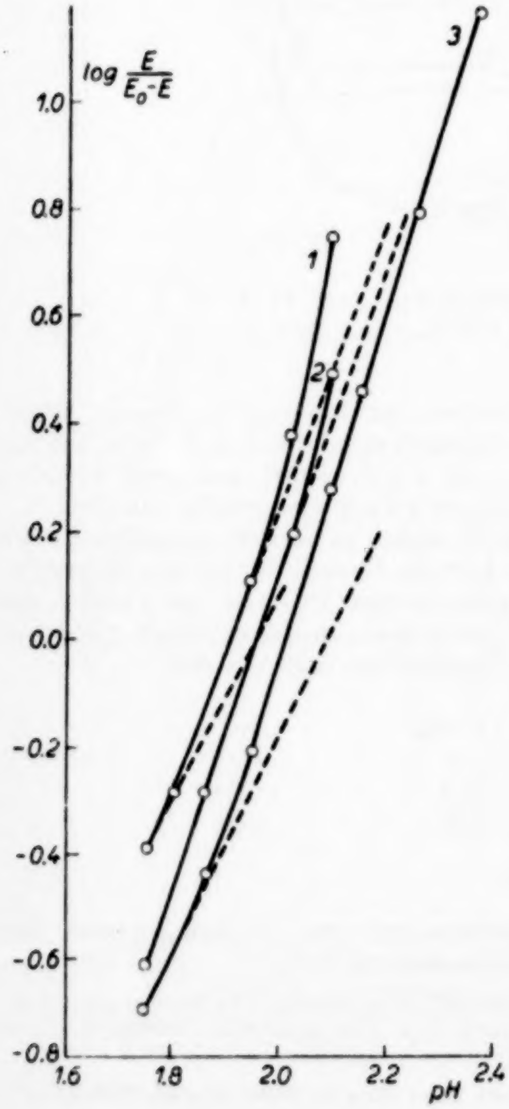

Fig. 3. Logarithmische Analyse des ersten steigenden Zweiges der pH-Kurve der Gallussäurekomplexe im pH-Gebiet 1.6-2.36.
Konstanter Reagenzüberschuss: $c = 2.123 \cdot 10^{-2} M$, $c_{\mathrm{Ti}} = 6.363 \cdot 10^{-5}\ M$, $\mu = 0.04$, Kurve 1: 500 mμ; 2: 470 mμ; 3: 430 mμ.

In diese Gleichungen wurden folgende Werte eingesetzt:

$$\mathrm{pH}_{1\text{-}2}\ 2.02 \pm 0.03 \quad \text{und} \log [\mathrm{RH_2}^-] = -4.05 \text{ (Punkt A)}$$
$$\mathrm{pH}_{2\text{-}3}\ 2.66 \pm 0.01 \quad \text{und} \log [\mathrm{RH_2}^-] = -3.41 \text{ (Punkt B)}$$

und die Bildungskonstanten ausgerechnet:

$$\begin{aligned} \log K_2 &= 0.01 \\ \log K_3 &= -1.91 \\ \hline \Delta\log K &= 1.92 \end{aligned}$$

Die Dissoziation der Gallussäure in der zweiten Stufe wurde vernachlässigt und ihre Konzentration in der Lösung ausgerechnet:

$$[\mathrm{RH_3}]_0 = [\mathrm{RH_3}] + [\mathrm{RH_2}^-].$$

Titankomplexe der Pyrogallolcarbonsäure

Die Absorptionskurven der orangen Ti-Lösungen mit Pyrogallolcarbonsäure weisen im ganzen pH-Gebiet 1.82-5.93 einen einheitlichen Charakter auf und bilden ein flaches Absorptionsmaximum bei 370-372 mμ (Fig. 4). Die sauren Lösungen mit einer niedrigen Pyrogallolcarbonsäure-Konzentration werden bald braun und die Extinktion sinkt ab.

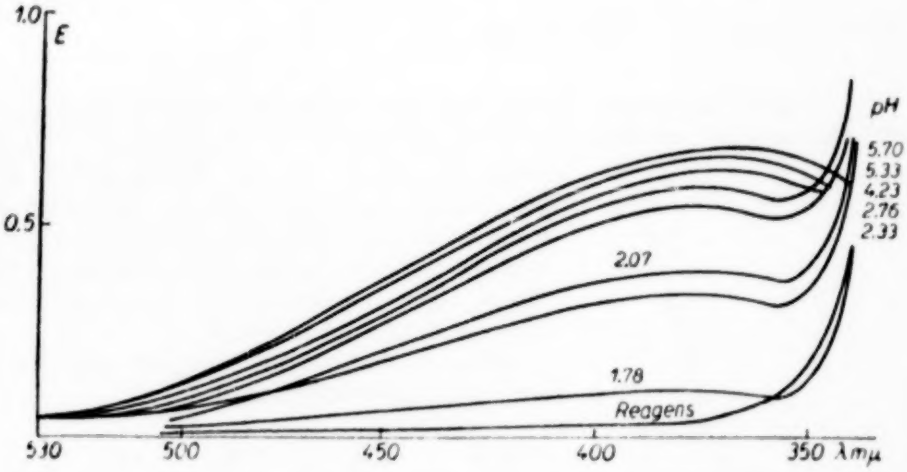

Fig. 4. Absorptionskurven der Komplexe der Pyrogallolcarbonsäure mit Ti^{+4}. $c_{\mathrm{Ti}} = 4.772 \cdot 10^{-5} M$, 10 ml 1% Lösung des Reagenzes in 0.1*N*-Natriumacetat.

Die pH-Kurven der Lösung bei einem Überschuss von Pyrogallolcarbonsäure für 500-430 mμ steigen von pH 1.5-2 scharf auf, und wenden sich zwischen pH 2.65-3.5 wagrecht um. Die Extinktion bleibt dann praktisch konstant bis pH 5.8 (Fig. 5). Für die Anzahl der bei der Komplexbildung abgespaltenen Protone im Gebiet des steigenden Astes der pH-Kurve führt die logarithmische Analyse zu den Werten:

λ mμ	*n*
430	2.72
470	2.82
500	2.93

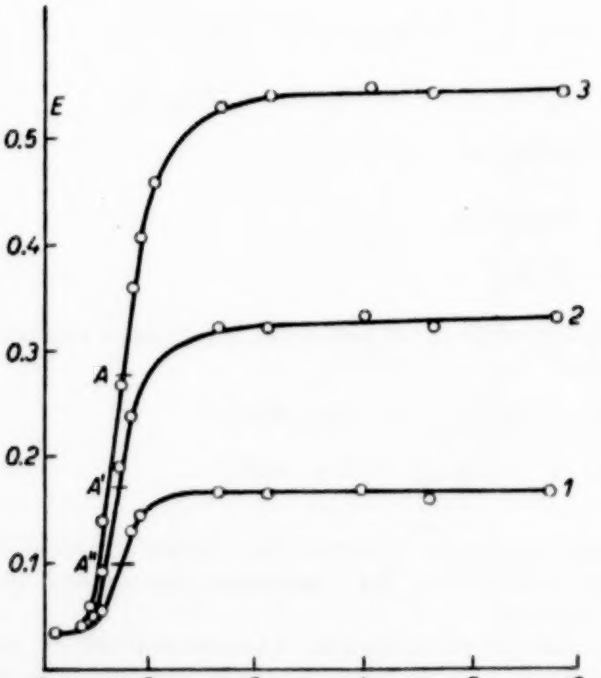

Fig. 5. pH-Kurven der Titankomplexe der Pyrogallolcarbonsäure.
$c_{\mathrm{Ti}} = 6.363 \cdot 10^{-5} M$, $\mu = 0.04$,
Konzentration der Pyrogallolcarbonsäure $10^{-2} M$.
Kurve 1: 500 mμ; 2: 470 mμ; 3: 430 mμ.

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Wenn zwei Hydroxylprotone gleichzeitig bei der Bildung des Komplexes (analog zu Pyrokatechin oder Sulfosalicylsäure) abgespalten werden, entsteht bei pH 1.5-2 ein Gemisch von Komplexen TiR und TiR_2 (Fig. 6). Der Letzte wird einheitlich bei pH 3.5-5.8 gebildet.

Für den Punkt A in den pH-Kurven (Fig. 5) ist $[TiR] = [TiR_2]$, bei $pH_{1-2} = 1.75 \pm 0.02$ und der Logarithmus der entsprechenden Bildungskonstante des Komplexes TiR_2 ist dann

$$\log K_2 = 2 \log[H_{1-2}] - \log[RH_2^-]$$
$$\log K_2 = -0.02$$

Die Pyrogallolcarbonsäure dissoziiert dabei in der ersten Stufe ($pK_1 = 3.26$), die Dissoziation des dritten Hydroxyls kann vernachlässigt werden. Die Gesamtkonzentration des Reagenzmittels ist dann $(H_3R)_0 = [H_3R] + [H_2R]$ und ergibt für $[H_3R]_0 = 1.06 \cdot 10^{-2} M$ den log $[RH_2^-] = -3.48$.

Die Ähnlichkeit der pH-Kurven der Ti-Komplexe der Gallussäure mit Pyrokatechin und die der Pyrogallolcarbonsäure mit Sulfosalicylsäure ist merkwürdig. Die Bindung mit Ti^{+4} kommt jedoch bei der Pyrogallolcarbonsäure wahrscheinlich über die beiden *o*-Phenol-Hydroxyle zu Stande. (Die Empfindlichkeit der Reaktion pD = 5.6 ist praktisch dieselbe, wie bei Pyrokatechin und Pyrogallol.) Die Carboxylgruppe stabilisiert sowohl das Reagenzmittel als auch den entstehenden Komplex.

Die Stufenbildungskonstanten für die Komplexe TiR konnten nicht berechnet werden, da der mol. Extinktionskoeffizient unbekannt ist. Der Übergang der Komplexe TiR/TiR_2 wird weder durch eine Welle an den pH-Kurven, noch durch einen isobestischen Punkt an den Absorptionskurven gedeutet.

Die Komplexe der Pyrogallolcarbonsäure und der Gallussäure werden weiterhin nach der Methode der kontinuierlichen Variationen in äquimolaren und nicht-äquimolaren Lösungen, und durch andere spektrophotometrischen Methoden studiert.

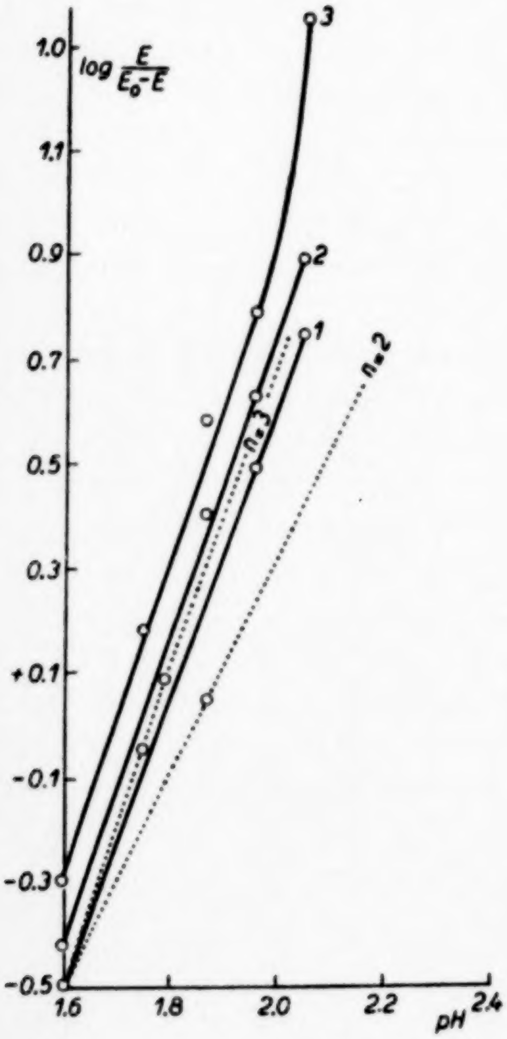

Fig. 6. Logarithmische Analyse der pH-Kurve der Pyrogallolcarbonsäurekomplexe mit Titan im pH-Gebiete 1.6-2.05.
$c_{Ti} = 6.363 \cdot 10^{-5} M$, $\mu = 0.04$, Konzentration der Pyrogallolcarbonsäure: $1.063 \cdot 10^{-3} M$ (Acetatpuffer).
Kurve 1: 430 mμ; 2: 470 mμ; 3: 500 mμ.

SCHLUSSFOLGERUNGEN

Aus dem Vergleich der Resultate bei verschiedenen Polyphenolen[9–12] können wir eine einheitliche Bildungsweise der Ti-Komplexe in Lösung ersehen. Die stufenweise Komplexbildung ist durch die Bildungskonstanten der zweiten und dritten Stufe angegeben.

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TABELLE II

DIE STUFENBILDUNGSKONSTANTEN EINIGER Ti-KOMPLEXE

Reagenz	*log K*			*Δlog K*
	TiR_2	*TiR_3*	*$TiOHR_3$*	
Chromotropsäure		1.14	—3.86	5.00
Gallussäure	0.01	—1.91		1.92
Pyrogallolcarbonsäure	—0.02			
Tiron	—2.22	—4.08		1.86
Pyrokatechin	—3.30	—4.90		1.60
Sulfosalicylsäure	—1.50			

In saurer Lösung und bei geringer Reagenzkonzentration bilden sich sehr dissoziierte Komplexe TiR, die bei wachsenden pH-Werten in stabilere Formen TiR_2 übergehen. Bei höheren pH-Werten und bei Anwesenheit des Reagenzüberschusses sind die stabilen Komplexformen TiR_3 am meisten bevorzugt. Nur bei der Sulfosalicylsäure und bei der Pyrogallolcarbonsäure wurde diese Stufe noch nicht bewiesen.

Besondere Stabilität und abnormale Farbe der Ti-Komplexe mit Chromotropsäure liegt in engem Zusammenhang mit der festen Wasserstoffbrücke der *peri*-Phenole, die durch einen Induktions- und Dipoleffekt der beiden Sulfogruppen stabilisiert wird. Das Verhalten erinnert in erster Annäherung an die Ungleichwertigkeit der Oximgruppen bei aliphatischen 1.2-Dioximen, wo auch das zweite Proton nur schwer abspaltbar ist.

Die fortschreitende Koordination der Phenole ist mit einer Verschiebung des Absorptionsmaximums nach kürzeren Wellenlängen verbunden. Eine ähnliche hypsochrome Wirkung wurde auch bei Eisenkomplexen mit *o*-Diphenolen[13], *o*-Phenolcarbonsäuren[14] und mit der Koji-Säure beobachtet[15], wo auch eine stufenartige Bildung von Komplexen bei verschiedenen pH-Werten nachgewiesen wurde. Die Ursache dieser Erscheinung kann man in der wachsenden Kontrapolarisationswirkung der stark polaren Me-O Bindung der koordinierenden Komplexbildner und in der wachsenden Symmetrie suchen.

Mit wachsender Stabilität der Titan-Chelate wurde eine bathochrome Verschiebung ihres Absorptionsmaximums im Zusammenhang mit dem wachsenden kovalenten Charakter der polaren Ti-O Bindung in einem fünf- oder sechsgliedrigen Chelatringe

TABELLE III

ABSORPTIONSMAXIMA DER TITANKOMPLEXE

Reagenz	*$\lambda_{max.}$ bei pH 4.5—5.5 mμ*	*Verschiebung des Absorptionsmaximums mμ*
1.8-Dioxynaphtalin	435	495—435
Chromotropsäure	420	472—420
Pyrokatechin	385	420—385
Tiron	380	420—380
Pyrogallolcarbonsäure	365—370	
Gallussäure	365	375—365
Dioxy-R-Säure	365	375—365
Salicylsäure	360	
Ascorbinsäure	360	
Mekonsäure	357	
Sulfosalicylsäure	357	
Acetylaceton	322	

beobachtet. Eine gleiche Erscheinung beobachtete SONE[16] bei Chelaten von Acetylaceton, Salicylaldehyd, Salicylaldoxim und Dimethylglyoxim.

Orange oder gelbe Verbindungen in schwach saurer Lösung liefern mit Ti^{+4} auch Oxy-γ-pyrone, Polyoxyflavonole, enolisierte 1.3-Diketone und Endiole. Die Ursache der grossen bathochromen Verschiebungen des Absorptionsmaximums der Komplexe mit 1.8-Dioxynaphtalin und Chromotropsäure liegt nicht in einer grossen Beweglichkeit der π-Elektronen und im Anelierungseffekt des Naphtalinskelettes, sondern in dem abnormal stabilen sechsgliedrigen Chelatringe. Dioxy-R-Säure liefert nur orange Komplexe mit Ti^{+4} mit Absorptionsmaximum 375-366 mμ.

Bemerkenswert ist eine grössere Stabilität des sechsgliedrigen Chelatringes der *peri*-Diphenole mit Ti^{+4} im Vergleich zu dem fünfgliedrigen Chelatring bei *o*-Diphenolen.

Die Gegenwart der $-SO_3H$ Gruppe in *m*-Stellung zur Hydroxylgruppe erhöht die Stabilität des entstehenden Chelates. Das Absorptionsmaximum des Komplexes ist jedoch nach kürzeren Wellenlängen verschoben (Tab. III). Einen schwächeren Einfluss übt die $-COOH$ Gruppe und auch ein weiterer kondensierter aromatischer Ring aus. Eine ähnliche Erscheinung wurde früher bei den Eisenkomplexen der Phenole[17] und auch bei den Acetylacetonaten beobachtet[18].

Die Reaktionen der Gallussäure und der Pyrogallolcarbonsäure mit Ti^{+4} gehören zu der Gruppe der Polyphenolreaktionen.

TABELLE IV

BEDINGUNGEN FÜR DIE QUANTITATIVE BILDUNG DER TITANKOMPLEXE

	pH	*Komplex*	λ *mμ*
Chromotropsäure	3.0—6.20	TiR_3, $TiOHR_3$	470*
	5.00—6.20	$TiOHR_3$	420
Pyrokatechin	3.5—6.4	(TiR_2), TiR_3	430—450*
Tiron	3.30—6.0	(TiR_2), TiR_3	430—450*
	4.0—6.0	TiR_3	430, 470
Sulfosalicylsäure	2.0—4.8	TiR_3	430
Gallussäure	3.3—5.6	(TiR_2), TiR_3	430
	3.5—5.8	TiR_3	430, 470
Pyrogallolcarbonsäure	3.5—5.8	TiR_2	430

* isobestischer Punkt

TABELLE V

MOLARE EXTINKTIONSKOEFFIZIENTEN DER KOMPLEXE

	Komplex	ε_m	λ *mμ*
Chromotropsäure	TiR_3	$1.223 \cdot 10^4$	470
	$TiOHR_3$	$1.790 \cdot 10^4$	430
1.8-Dioxynaphtalin		$1.031 \cdot 10^4$	495
		$1.596 \cdot 10^4$	435
Salicylsäure		$1.309 \cdot 10^4$	360
Gallussäure	TiR_2	$1.031 \cdot 10^4$	430
	TiR_3	$1.100 \cdot 10^4$	430
Pyrogallolcarbonsäure	TiR_2	$8.377 \cdot 10^3$	430
Tiron	TiR_2	$8.172 \cdot 10^3$	430
	TiR_3	$8.780 \cdot 10^3$	430
Pyrokatechin	TiR_2	$6.223 \cdot 10^3$	430
	TiR_3	$7.170 \cdot 10^3$	430
Sulfosalicylsäure	TiR_2	$2.583 \cdot 10^3$	430

Für die Ausarbeitung einer exakten photometrischen Methode bei dieser Gruppe von Reaktionen müssen wir die Bedingungen der Bildung eines einheitlichen und stabilen Komplexes finden. Sie sind am besten durch die wagrechten Äste der pH-Kurve bei konstantem Reagenzüberschuss zu beurteilen (Tab. IV).

Die photometrische Bestimmung von Ti^{+4} durch Sulfosalicylsäure im sichtbaren Gebiet[19] ist infolge der geringen Stabilität des entstehenden Komplexes TiR_2 und des sehr niedrigen molaren Extinktionskoeffizienten im sichtbaren Teil des Spektrums wenig vorteilhaft.

Von Vorteil ist die Bestimmung des Titans mit Hilfe der Gallussäure[20] *und des Tirons*[21] *bei 430 mμ.* Die Reagenzien sind gegenüber der Oxydation relativ stabil, die färbigen Lösungen weisen eine hohe Extinktion auf, die in einem weiten pH-Gebiet konstant ist. Bei der Pyrogallolcarbonsäure stört ein wenig ihre verhältnismässig geringe Widerstandsfähigkeit gegenüber der Oxydation.

Bei der *Anwendung der Chromotropsäure zur Titanbestimmung*[22] begegnet man einigen Schwierigkeiten. Die Extinktion von farbigen Lösungen ist im weiten pH-Gebiet 3.6-6.20 konstant. Ein leichter gegenseitiger Übergang des roten Komplexes TiR_3 in den orangen Komplex $TiOHR_3$ erfordert aber eine Messung bei 467-470 mμ, wo beide Komplexe denselben molaren Extinktionskoeffizient haben. Ein wenig stört auch die eigene Färbung der Chromotropsäure und die Notwendigkeit frisch bereitete Lösungen zu verwenden. Die Lösungen des Dinatriumsalzes sind leicht oxydierbar und schwierig zu reinigen.

ZUSAMMENFASSUNG

In den Lösungen der farbigen Titankomplexe mit Chromotropsäure, Pyrokatechin, Tiron, Sulfosalicylsäure, Pyrogallolcarbonsäure und Gallussäure wurde spektrophotometrisch eine stufenweise Komplexbildung nachgewiesen. In verdünnten sauren Lösungen bildet sich gewöhnlich ein einfacher Komplex TiR, in schwach sauren Pufferlösungen ein relativ stabiler Komplex TiR_3, welcher bisher nur bei der Sulfosalicylsäure und Pyrogallolcarbonsäure nicht nachgewiesen wurde. Die Stabilität der entstandenen Chelatbindung hängt direkt mit der Stabilität der Wasserstoffbindung zwischen den funktionellen Gruppen des Chelatbildners sowie auch mit den Absorptionsspektren des Chelates zusammen. Wenn man eine exakte photometrische Bestimmungsmethode ausarbeiten will, ist die Bildung eines stabilen einheitlichen Komplexes eine notwendige Bedingung. Von diesem Standpunkte werden einige Methoden der photometrischen Titanbestimmung beurteilt.

SUMMARY

The stepwise formation of complexes was demonstrated spectrophotometrically in solutions containing coloured complexes of titanium with chromotropic acid, pyrocatechol, tiron, sulfosalicylic acid, gallic acid and pyrogallolcarboxylic acid in acid medium. In dilute acid solutions of complexes a simple complex TiR is usually formed, in weakly acid buffer solutions a relatively stable complex TiR_3 is formed, which, however, up till now has not been demonstrated in the case of sulfosalicylic and pyrogallolcarboxylic acid. The stability of the chelates formed is directly related to their absorption spectra and the hydrogen bond stability between the functional groups of the ligand. Formation of a simple stable complex is a necessary condition for the development of an exact photometric method. From this point of view some methods for determination of titanium have been discussed.

RÉSUMÉ

Les auteurs ont montré par spectrophotométrie la formation graduelle des complexes du titane avec les réactifs suivants, en solution: acide chromotropique, pyrocatéchine, tiron, acides sulfosalicylique, gallique et pyrogallolcarboxylique. Dans les solutions acides et peu concentrées,

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il se forme généralement un simple complexe, TiR; dans les solutions très peu acides, tamponnées, il se forme enfin un complexe relativement plus stable TiR_3 qui, avec les acides sulfosalicylique et pyrogallolcarboxylique, n'était pas encore connu. La stabilité de ces chélates du titane dépend directement de la stabilité de la liaison hydrogène entre les groupements fonctionnels des réactifs, ainsi que des spectres d'absorption des chélates. Pour établir une méthode exacte de dosage photométrique, il faut rechercher les conditions de formation d'un complexe unique et stable. Quelques méthodes photométriques de dosage du titane ont été examinées de ce point de vue.

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SPECTROPHOTOMETRIC DETERMINATION OF RARE EARTH MIXTURES*

by

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INTRODUCTION

The analysis of rare earth mixtures is a problem which is not readily handled by gravimetric or titrimetric methods. The possibility of using the characteristic absorption spectra of the rare earth elements for quantitative analysis has been recognized for many years[1,2]. The development of such methods was delayed primarily because of high instrumentation cost. With the advent of moderately priced spectrophotometers these elements began to be studied in the various acid media. RODDEN[3] studied the rare earth nitrates, STEWART[4] the perchlorates, MOELLER AND BRANTLEY[5] the chlorides, nitrates, perchlorates, and acetates, and HOLLECK AND HARTINGER[6] the chlorides.

The molar absorptivities reported to date have been only partially correct as a result of poorer instrument sensitivity and resolution than is now available.

MATERIALS AND APPARATUS

Rare earths. The pure rare earths used for this work were separated by ion exchange at this laboratory and were analysed spectrographically and found to be at least 99.9 per cent pure.

Perchloric acid. The 1 M perchloric acid was prepared by dilution from 72% reagent-grade stock.

Glassware. The glassware used was Kimble Normax and Pyrex class "A".

Spectrophotometers. The general absorption spectra in Figs. 1 through 13 were obtained with a Cary Model 14 recording spectrophotometer. Analyses were made by measuring the individual absorption bands with a Beckman Model DU quartz spectrophotometer with photomultiplier attachment. A slide rule hairline glass was cemented on the glass windows above the wavelength and absorbance dials to decrease the error due to parallax. The wavelength scale was calibrated against mercury lines. A hydrogen lamp and silica cells were used below 375 mμ.

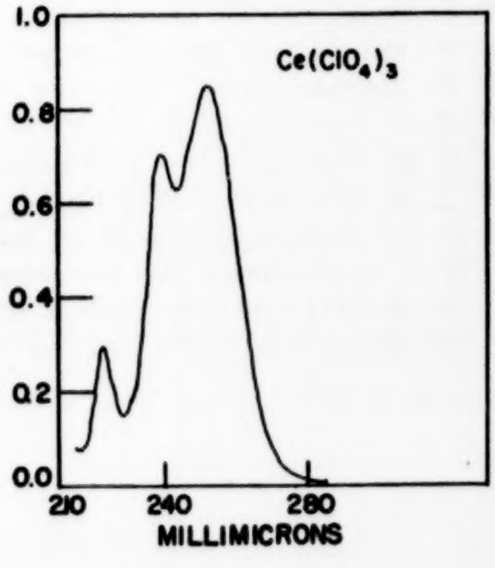

Fig. 1. Cerium: 0.002 g CeO_2 diluted to 10 ml, 1-cm cell.

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* Contribution No. 453. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

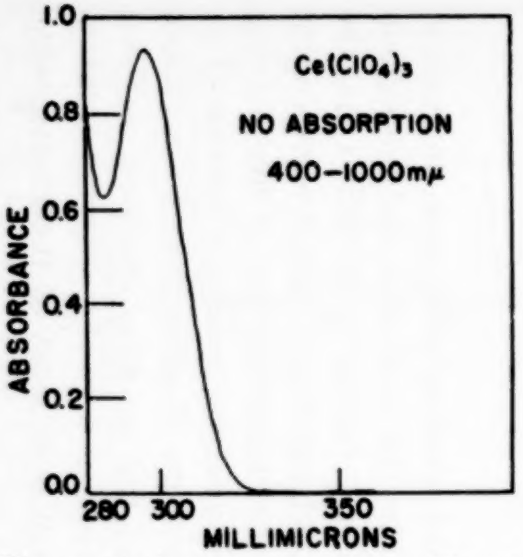

Fig. 2. Cerium: 0.1 g CeO_2 diluted to 10 ml, 1-cm cell.

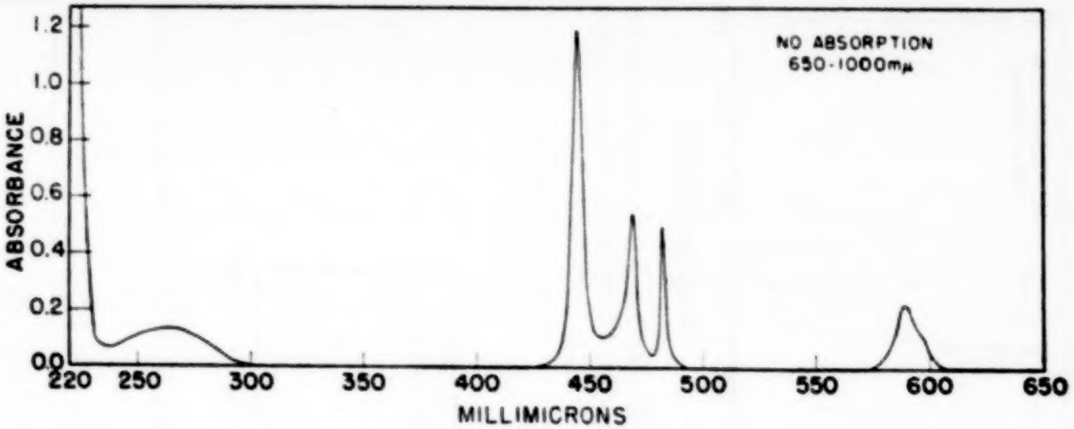

Fig. 3. Praseodymium: 0.2 g Pr_6O_{11} dissolved in and diluted to 10 ml with 1*M* perchloric acid, 1-cm cell.

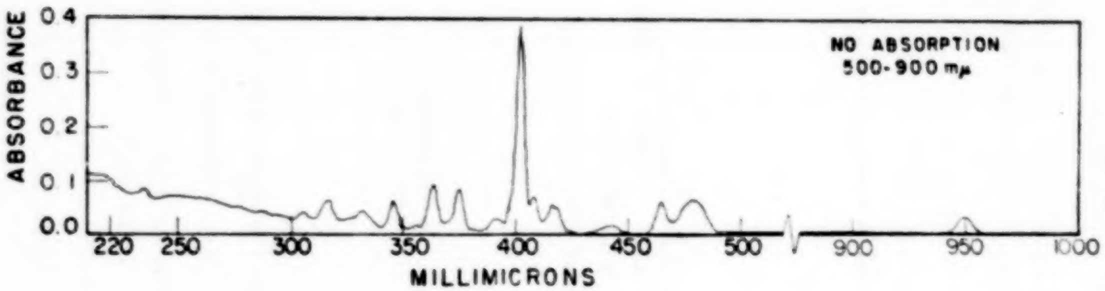

Fig. 5. Samarium: 0.2 g Sm_2O_3 dissolved in and diluted to 10 ml with 1*M* perchloric acid, 1-cm cell.

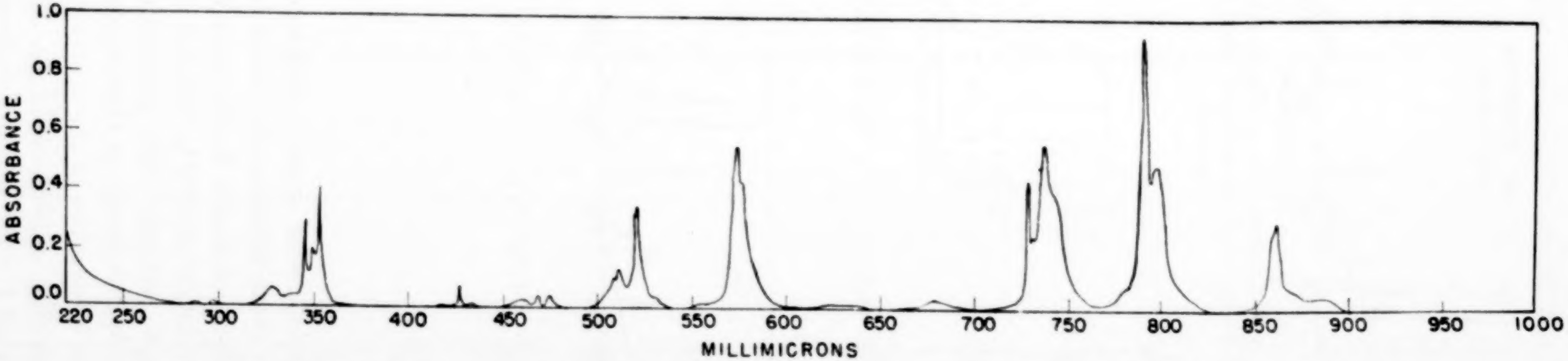

Fig. 4. Neodymium: 0.2 g Nd_2O_3 dissolved in and diluted to 10 ml with 1*M* perchloric acid, 1-cm cell.

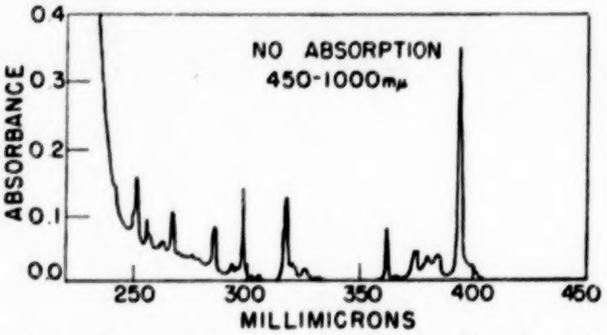

Fig. 6. Europium: 0.2 g Eu_2O_3 dissolved in and diluted to 10 ml with 1 *M* perchloric acid, 1-cm cell.

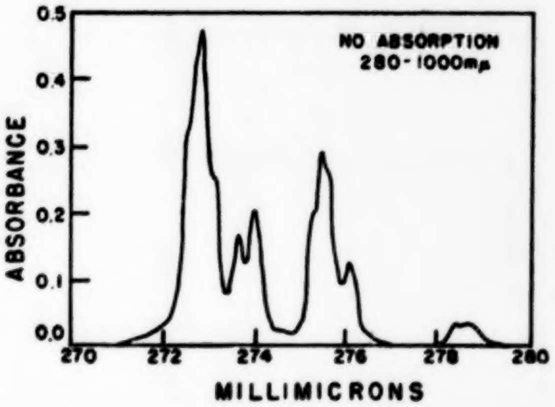

Fig. 7. Gadolinium: 0.2 g Gd_2O_3 dissolved in and diluted to 10 ml with 1 *M* perchloric acid, 1-cm cell.

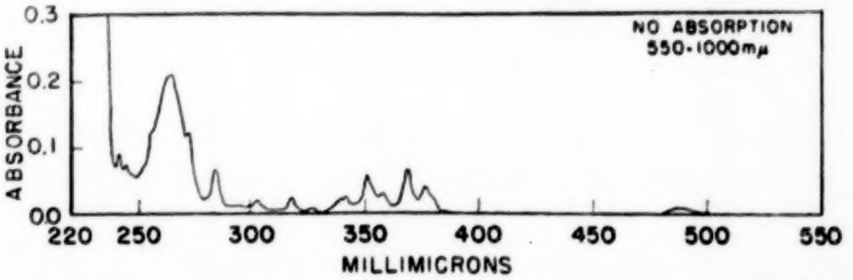

Fig. 8. Terbium: 0.2 g Tb_4O_7 dissolved in and diluted to 10 ml with 1 *M* perchloric acid, 5-cm cell.

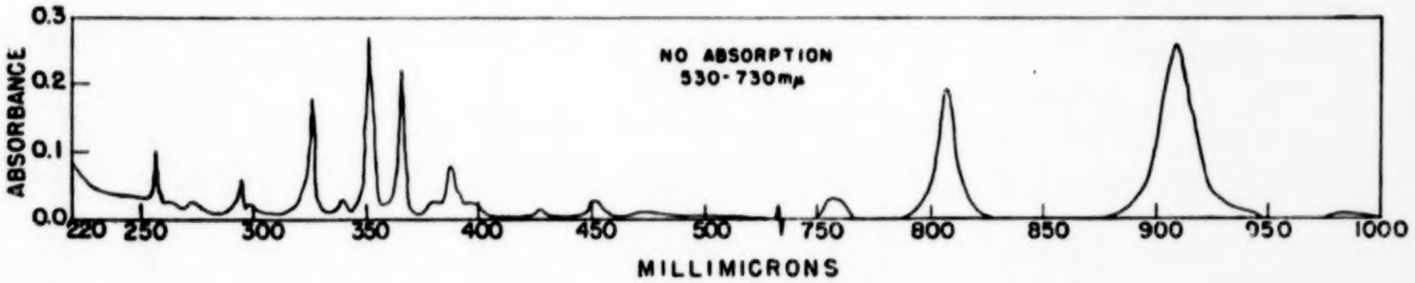

Fig. 9. Dysprosium: 0.2 g Dy_2O_3 dissolved in and diluted to 10 ml with 1 *M* perchloric acid, 1-cm cell.

DISCUSSION

Selection of media. This laboratory has practiced spectrophotometric analysis of rare earth mixtures for about ten years as a control for the separation and production of these elements. Early work was done in hydrochloric acid but it was found that the dissolution of Pr_6O_{11} yielded chlorine which gives a large absorbance at wavelengths below 420 mμ. This absorption interfered with the determination of ions having absorption bands at these lower wavelengths. Nitric acid was ruled out because of its high absorption in the ultraviolet region of the spectrum. Perchloric acid was chosen since the oxides could be dissolved directly and the solution analysed without further treatment for interferences. There is no problem with the reference solution since perchloric acid has no appreciable absorption over most of the useful range of the spectrum.

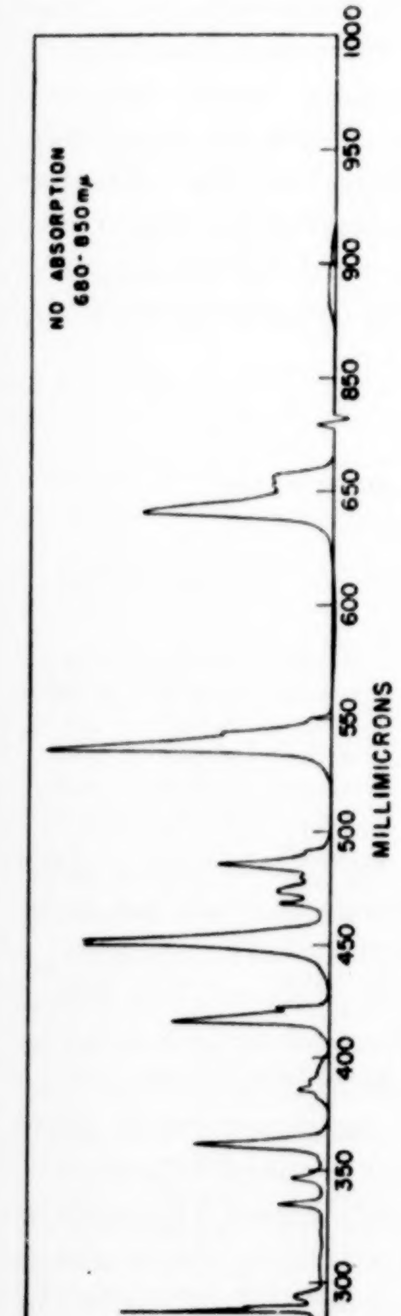

Fig. 10. Holmium: 0.2 g Ho_2O_3 dissolved in and diluted to 10 ml with 1 *M* perchloric acid, 1-cm cell.

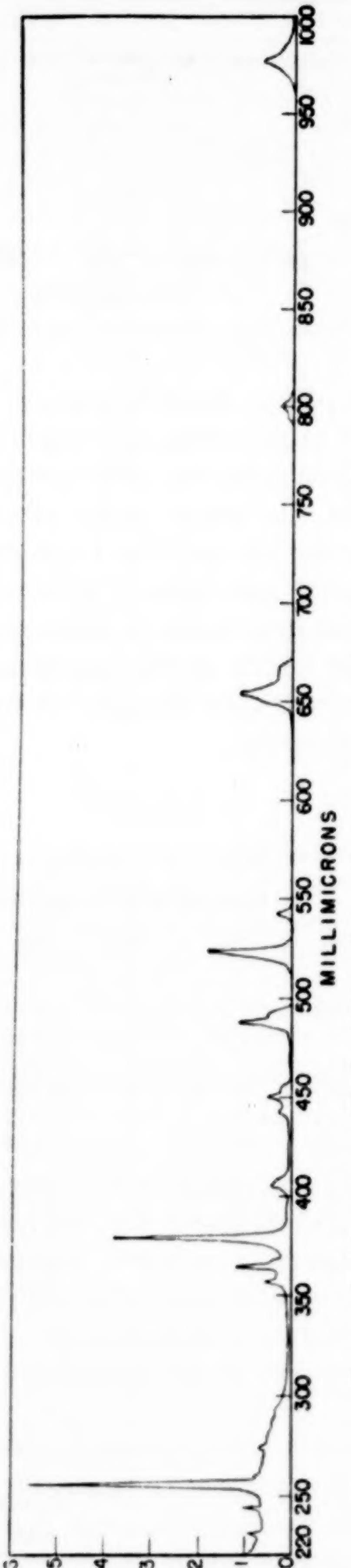

Fig. 11. Erbium: 0.1 g Er_2O_3 dissolved in and diluted to 10 ml with 1 *M* perchloric acid, 1-cm cell.

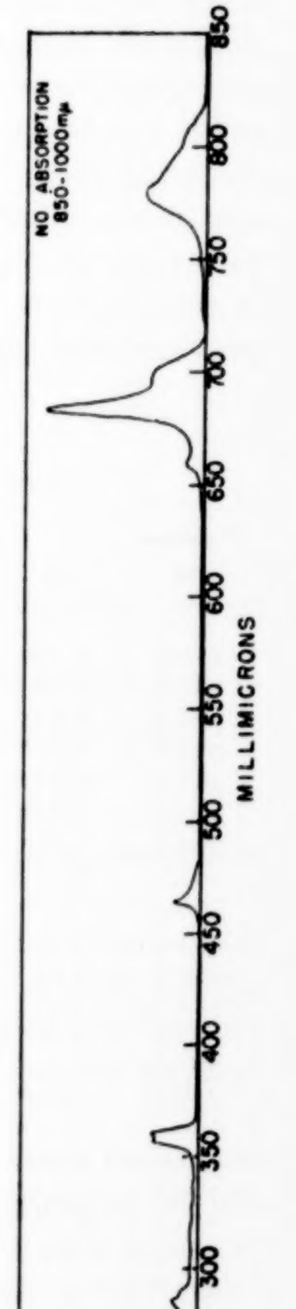

Fig. 12. Thulium: 0.2 g Tm_2O_3 dissolved in and diluted to 10 ml with 1 *M* perchloric acid, 1-cm cell.

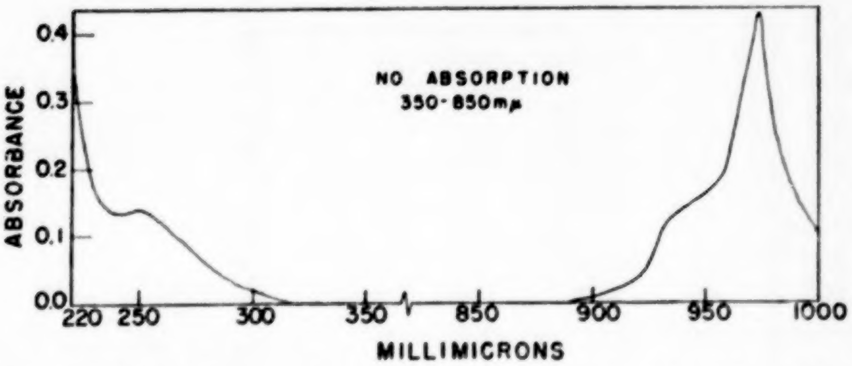

Fig. 13. Ytterbium: 0.2 g Yb_2O_3 dissolved in and diluted to 10 ml with 1 *M* perchloric acid, 2-cm cell.

Molar absorptivities. The molar absorptivities, ε, reported in Table I are those observed on the Cary Model 14 recording spectrophotometer. In many instances these values are higher than those reported by other authors. The increased dispersion of this instrument accounts for the larger molar absorptivity since nearly all rare earth bands are extremely narrow and few instruments are capable of completely resolving them. This property and others such as sensitivity of the detector and intensity of the light source make it necessary to determine the molar absorptivity at a minimum slit width on the instrument to be used for the analysis. A good analysis can be reported even though the band is not completely resolved, provided the slit width is constant.

TABLE I

MOLAR ABSORPTIVITIES FROM CARY MODEL 14 SPECTROPHOTOMETER

Wavelength mμ	*Molar absorptivities, liters/mole-centimeter*									
	Nd	*Pr*	*Sm*	*Eu*	*Gd*	*Dy*	*Ho*	*Er*	*Tm*	*Yb*
272.8	0.210	1.13	0.166	0.335	4.20	0.215	0.227	0.698	0.685	0.365
287.0	0.185	0.511	—	0.132	—	0.140	3.59*	0.316	0.521	0.266
350.4	2.60	—	0.052	—	—	2.54*	0.057	0.096	0.145	—
354.0	5.20*	—	0.087	—	—	0.737	0.047	0.382	0.454	—
361.1	0.042	—	0.453	0.053	—	0.271	2.34*	0.296	0.801	—
365.0	0.025	—	0.244	0.062	—	2.10*	0.331	1.94	0.154	—
379.6	0.067	—	0.052	0.299	—	0.252	0.047	7.18*	—	—
394.2	0.025	—	0.148	3.06*	—	0.233	0.123	0.096	—	—
401.5	—	—	3.31*	0.097	—	0.187	0.038	0.086	—	—
444.2	—	10.49*	0.044	—	—	0.047	0.454	0.306	—	—
450.8	0.025	1.29	—	—	—	0.261	4.16	0.497	—	—
521.6	4.41*	—	—	—	—	—	0.047	2.10	—	—
523.5	1.68	—	—	—	—	—	0.076	3.20*	—	—
537.0	—	—	—	—	—	—	5.16*	0.076	—	—
575.5	6.93*	0.102	—	—	—	—	—	—	—	—
640.4	—	—	—	—	—	—	3.53*	0.153	—	—
683.0	0.336	—	—	—	—	—	—	—	2.56*	—
739.5	7.20*	—	—	—	—	—	—	—	0.058	—
794.0	11.78*	—	—	—	—	0.084	—	0.143	0.579	—
908.0	—	—	—	—	—	2.46*	0.113	—	—	0.089
974.0	—	—	0.052	—	—	0.047	—	1.29	—	2.12*

* Analytically significant absorption bands.

The molar absorptivities reported in Table II are typical values from a standard Beckman Model DU spectrophotometer and a Beckman Model DU spectrophotometer

TABLE II

MOLAR ABSORPTIVITIES FROM BECKMAN MODEL DU SPECTROPHOTOMETER

Rare Earth	*Wavelength mμ*	*Without photomultiplier*		*With photomultiplier**
		Slit width mm	*ε, liters/mole-cm*	*ε, liters/mole-cm*
Nd	354.0	0.020		5.05
	521.6	0.020	4.29	4.29
	575.5	0.020	6.93	6.93
	739.5	0.020	7.03	
	794.0	0.020	9.96	
Pr	444.2	0.020	10.31	10.31
Sm	401.5	0.035	3.23	3.31
Eu	394.2	0.045	2.91	3.01
Gd	272.8	0.020		3.35
Dy	350.4	0.020		2.52
	365.0	0.020		2.05
	908.0	0.020	2.38	
Ho	287.0	0.020		3.31
	361.1	0.020		2.18
	450.8	0.020	4.00	4.00
	537.0	0.020	4.58	4.58
	690.4	0.020	3.05	3.05
Er	379.6	0.055	6.57	6.93
	523.5	0.020	3.20	3.20
Tm	683.0	0.030	2.56	
Yb	908.0	0.020	1.97	

* Slit width was 0.02 mm for each case when photomultiplier attachment was used.

with a photomultiplier attachment. These data are suitable for use as standards provided the experimental conditions are duplicated.

Mixtures. The analysis of rare earth mixtures depends on the separation of the bands and the ability of the instrument to resolve these sharp bands. A wide variety of mixtures can be analysed even though some interference is observed for certain rare earth mixtures. However, absorption bands can generally be selected so that these interferences are small.

Cerium. Cerium is not readily determined spectrophotometrically since the molar absorptivity varies with temperature and ionic strength[7]. Ceria is difficultly soluble in one molar perchloric acid. When more concentrated acid and hydrogen peroxide are used for dissolution the ionic strength varies and excess peroxide gives an absorbance interference.

Gadolinium. It is nearly impossible to determine gadolinium in a solution containing cerium since the molar absorptivity of cerium is two hundred times that of gadolinium. If gadolinium must be determined in the presence of cerium the solution should be diluted so that the absorbance can be conveniently determined. A background correction for cerium is estimated by extrapolation between absorbances determined on both sides of the gadolinium absorption band.

Samarium. If present in solutions to be analysed for samarium, cerium should be reduced with a sligth excess of hydrogen peroxide. This eliminates the cerium interference in the lower visible region of the spectrum.

Terbium. Terbium is not usually determined since the molar absorptivity is very low and the bands occur in the ultraviolet region of the spectrum where large interferences from other rare earths are observed.

Yttrium, Lanthanum, and Lutetium. These three ions have no absorption spectra over the wavelength range from 200-1000 mμ.

RECOMMENDED PROCEDURE

Selection of Instrument. The standard Beckman DU spectrophotometer is suitable for the determination of the rare earths other than gadolinium. This instrument is not satisfactory for measurement of rare earth absorption bands at wavelengths lower than 400 mμ. The intensity of the light source decreases for wavelengths less than 400 mμ, which requires that the slit width be increased with a concomitant loss in resolution. However, if the instrument is equipped with a photomultiplier attachment the entire range from 250 mμ to 600 mμ is usable since a slit width of 0.02 mm can be maintained throughout. This will not completely resolve all the bands but it will give very satisfactory results.

The Cary Model 14 recording spectrophotometer has such good dispersion that complete resolution of the rare earth bands can be attained easily. Therefore no special precautions are necessary with this instrument.

If other instruments are considered for rare earth analysis the dispersion and sensitivity can be compared with that for the Beckman Model DU for a qualitative measure of the accuracy possible.

Analysis. The rare earths are precipitated as the oxalates and ignited at 900° C to the oxides. A 0.2 g weighed sample of the freshly ignited oxide is dissolved in and diluted to volume with 1 *M* perchloric acid in a 10-ml volumetric flask. Of course, more concentrated acid may be used for dissolving the samples but it is recommended that the diluted solutions be 1 *M* in perchloric acid.

The absorbance of this solution is determined at the appropriate wavelengths using 1-cm cells. The setting of the wavelength dial is the most critical part of this procedure. Since the wavelength calibration may be slightly in error and since there is a small amount of mechanical error inherent in the instrument, the following technique is recommended for setting the wavelength. The wavelength dial is set at the recommended wavelength for the element to be determined. The sample, having an absorbance of 0.2 or higher, is placed in the cell compartment and its absorbance is measured. With the shutter open the wavelength dial is very carefully adjusted until maximum absorbance is indicated by a maximum deflection. Adjustment of the absorbance dial may be necessary during the process. By this method the instrument may be set on the desired wavelength without the necessity of accurate and frequent wavelength calibration.

It is extremely important that the best spectrophotometric techniques be used for these analyses. The cells must be positioned and oriented in the cell holder the same each time. Larger cells may be used for greater sensitivity of minor constituents.

The accuracy of the analysis varies with molar absorptivity, cell length and concentration. In general, the limiting error is the precision of the instrument. The standard Beckman DU can be read with a precision of 0.002 absorbance unit, and with the photomultiplier attachment, it can be read with a precision of 0.001 absorbance unit. This gives an absolute error for this method of from 0.2-1.0 per cent.

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to Dr. F. H. SPEDDING and his rare earth group for supplying the pure rare earth oxides used in this study. We also wish to thank Dr. V. A. FASSEL for spectrographically analysing the various rare earth oxides for other rare earth impurities.

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SUMMARY

The molar absorptivities for most of the rare earths have been determined at the wavelengths of the various analytically significant absorption bands. These molar absorptivities have been determined on the Beckman Model DU spectrophotometer with and without a photomultiplier attachment as well as on a Cary Model 14 recording spectrophotometer. The techniques and instrumentation necessary for the satisfactory analysis of rare earth mixtures are discussed. A general procedure is presented which has been found most useful for the routine analysis of a wide variety of rare earth mixtures.

RÉSUMÉ

L'absorptivité moléculaire de la plupart des terres rares a été déterminée aux longueurs d'onde des bandes d'absorption significatives du point de vue analytique. Ces déterminations ont été effectuées à l'aide d'un spectrophotomètre Beckman modèle DU, avec ou sans appareil auxiliaire avec multiplicateur à émission secondaire de même qu'au moyen d'un spectrophotomètre enregistreur Cary modèle 14. Les techniques et l'appareillage nécessaires pour obtenir des analyses satisfaisantes de mélanges de terres rares sont discutées. Une méthode générale est décrite; elle s'est montrée très utile pour des analyses en série d'une grande variété de mélanges de terres rares.

ZUSAMMENFASSUNG

Die molekulare Absorption der meisten seltenen Erden wurde bei den Wellenlängen der verschiedenen analytisch wichtigen Absorptionsbanden bestimmt. Diese Bestimmungen wurden mit einem Beckman-Spektrophotometer Modell DU mit oder ohne Sekundärelektronenvervielfacher-Zusatzgerät und mit einem Cary-Registrierspektrophotometer Modell 14 ausgeführt. Die zur Ausführung befriedigender Analysen von Gemischen seltener Erden erforderlichen Verfahren und Apparate werden erörtert. Eine allgemeine Methode, die sich zur Ausführung von Routineanalysen sehr verschiedener Gemische von seltenen Erden besonders nützlich erwiesen hat, wird beschrieben.

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THE COLORIMETRIC DETERMINATION OF IRIDIUM BY *O*-DIANISIDINE

by

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There have been comparatively few procedures recommended for the colorimetric determination of iridium. Of four that have been developed usefully, three[1,5,6] are relatively insensitive compared to the fourth[8]; all four involve heating iridium solutions with various colour-forming reagents, and our experience has shown that the temperature and duration of heating may considerably influence the precision attainable. In this communication we describe a simple procedure that we have found useful for determining small amounts of iridium after isolation from other platinum metals.

When *o*-dianisidine in acetone is added to an acidic solution of chloroiridate(IV) a bright red solution is formed, the colour of which slowly fades. However, if the solution is only slightly acidic ($\text{pH} > 3$) a green solution is formed when the reagent is added which quickly changes to orange. If this orange solution is acidified with concentrated hydrochloric acid an intensely coloured purple solution is formed which is quite stable. This purple solution possesses a spectrum with an absorbance maximum at 530 mμ when measured against a reagent blank (Fig. 1).

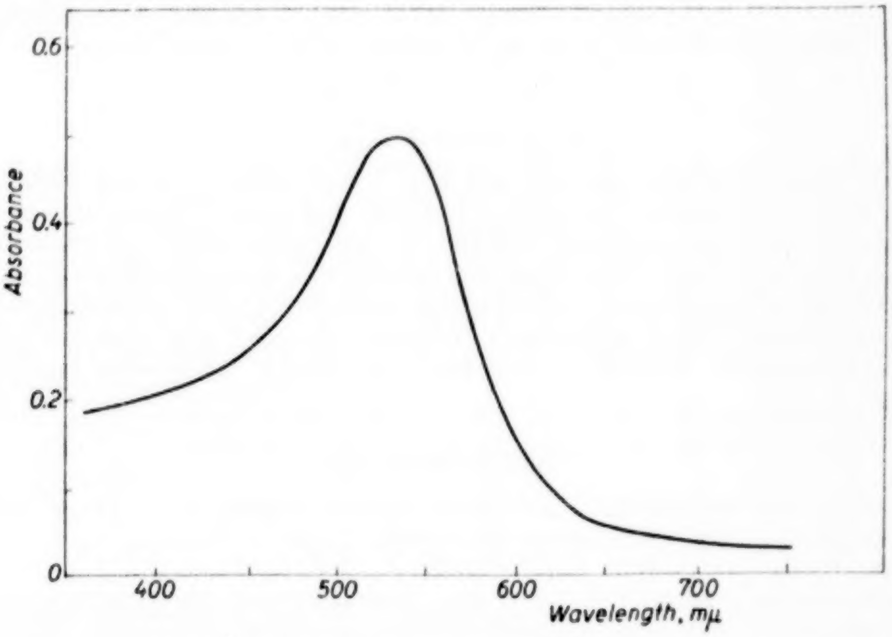

Fig. 1. Spectral curve for iridium(IV) solution with *o*-dianisidine (8 p.p.m. Ir).

We have no experimental basis for speculation concerning the reactions to which these colour changes correspond, but it seems likely that an oxidation of the organic base is one step. Consequently, interference by oxidizing agents, as well as by the other platinum metals, rather restricts the application of the method. It is a fact, however, that few specific colorimetric reagents for platinum metals have been discovered. The recent development of various physical methods of separation, for instance by partition chromatography[4] or by ion exchange[2,3], has made it easier to isolate small amounts of iridium than before, but there is still need for a simple sensitive means for its determination.

EXPERIMENTAL

Photometric measurements were made with a Klett-Summerson photoelectric colorimeter and optically matched test tubes, except for the examination of the spectral curve of the coloured solution which was made with a Beckman Model DK recording spectrophotometer. In the colorimeter a narrow-band filter (Lumetron No. 550) was used.

A stock solution of pure ammonium chloroiridate(IV) in $0.05M$ hydrochloric acid was prepared, and standardized by potentiometric titration with iron(II) sulphate[7]. This stock solution, which contained 1.89 mg of iridium per ml was diluted fifty-fold for the experiments described below. A 0.5% solution (w/v) of *o*-dianisidine (British Drug Houses) was prepared in acetone. This solution was quite stable and showed no change on prolonged standing. A $0.1M$ acetic acid-sodium acetate buffer of pH 4.7 was prepared by mixing equal volumes of $0.2M$ acetic acid and $0.2M$ sodium acetate. All chemicals used were of analytical reagent or C.P. grade.

Development of the basic procedure

In experiments to find optimum conditions for the colour reaction the following basic procedure was followed. A solution containing 189 μg of iridium was transferred to a 25-ml volumetric flask, and *o*-dianisidine solution and buffer solution were added. The sample was then made up to volume with $12M$ hydrochloric acid, and the absorbance measured.

The reaction did not proceed if the pH of the iridium solution was less than 3. Addition of 1 ml of *o*-dianisidine solution, which is basic, raised the pH of an iridium solution that was originally 3 to 4.3. The absorbance of the solution increased slightly with increasing pH, but at the same time the precision fell off, perhaps owing to partial hydrolysis of the chloroiridate solution. With an acetic acid-sodium acetate buffer of pH 4.7 iridium could be determined with maximum sensitivity consistent with good precision.

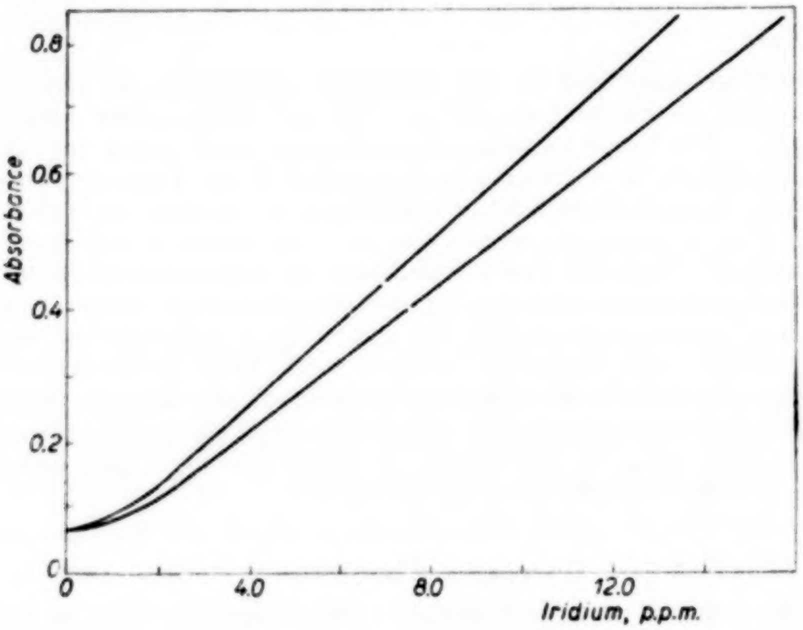

Fig. 2. Absorbance *vs.* concentration for iridium(IV) solutions with *o*-dianisidine.
A. Stock iridium solutions.
B. Acid iridium solutions.

The absorbance, measured against a reagent blank, varied with the quantity of reagent added but was a maximum for 0.75 to 1.0 ml of the 0.5% *o*-dianisidine reagent solution. One ml was chosen for all subsequent determinations.

A blank prepared with the *o*-dianisidine reagent showed a constant absorbance at 550 mμ when measured against a water blank. On the grounds of convenience we decided to make all measurements of absorbance of iridium solutions against a water blank.

Beer's law is followed from 2 to 20 μg per ml. A concentration of 17 μg per ml represents approximately unit absorbance. Below a concentration of 2 μg per ml there is little change of absorbance with change of concentration of iridium. This is shown in Fig. 2. These curves were plotted from data obtained with a water blank; the absorbance due to the *o*-dianisidine blank is given by the intercept on the vertical axis. Curiously enough, if the straight-line portion of the curve is extrapolated to zero concentration of iridium it passes through the origin.

Five replicate samples, each containing 189 μg of iridium in a final volume of 25 ml, gave a mean absorbance of 0.478 with an average deviation of 0.0004 or 0.08%. No change in the absorbance of these solutions was found after 96 hours.

Interferences

Palladium, platinum, rhodium, nickel, chromium, and copper were found to interfere with the colour development when present with iridium in acidic solutions. The absorbance in each case, except for platinum, was smaller than for the same amount of iridium alone. Rhodium produced the least interference; with 25 μg of rhodium the absorbance due to 189 μg of iridium was lowered by one per cent. Oxidizing agents such as iron(III), gold(III), and nitric acid must be absent.

Treatment of acidic samples

Since iridium is usually present in acidic solutions provision must be made to remove the acid while retaining the iridium in the quadrivalent state. This was not possible for sulphuric acid solutions, but was achieved for hydrochloric acid solutions by evaporating with a small amount of nitric acid and sodium chloride and then twice with hydrochloric acid. The sodium chloride kept

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the iridium from baking onto the glass beaker during evaporation. When the residue from this treatment was taken up in water and treated by the procedure already described the absorbance was found to be smaller than that obtained for equivalent amounts of the stock solution. Thus five replicate samples, each containing 189 μg of iridium, gave a mean absorbance of 0.386 with an average deviation of 0.0006 or 0.16%. The absorbance of these samples conformed to Beer's law for concentrations above 2 μg per ml (Fig. 2), and was independent of the amount of acid present in the original iridium solution. We were unable to assign a cause for the decrease in molar absorptivity of the solutions that had been subjected to this evaporation. We judged from the high precision obtainable that this decrease could not be due to reduction of a portion of the iridium from the quadrivalent state. We did ascertain that the amount of sodium chloride introduced in the recommended procedure caused no measurable decrease in colour of the solution.

Recommended procedure

In view of our findings described in the preceding paragraph we decided to evaporate all samples to dryness before developing the colour. The following is our complete procedure.

Add to each sample a few drops of concentrated nitric acid and 1 ml of a 0.2% solution of sodium chloride. Evaporate to dryness on a boiling-water bath. Take up the residues three times in a few drops of dilute hydrochloric acid, evaporating to dryness each time before adding the next portion of acid. This evaporation eliminates the last traces of nitric acid which, if present, would oxidize the reagent. Dissolve the evaporated residues in a small volume of water and transfer to 25-ml volumetric flasks, diluting to volume with water. After mixing these solutions, transfer 5 ml aliquots to 25-ml volumetric flasks. Add 1 ml of *o*-dianisidine reagent, 2 ml of acetic acid-sodium acetate buffer, and dilute to volume with 12*M* hydrochloric acid. Measure the absorbance at 530 mμ (or with a filter having approximately this wave-length for maximum transmission) against a distilled water blank. It is permissible to develop the colour in the samples resulting from evaporation (that is, not taking aliquots) provided that these are transferred to volumetric flasks in a total volume of 5 ml of water.

ACKNOWLEDGEMENT

We are grateful for a grant in aid of this research from the Ontario Research Foundation and previously the Research Council of Ontario.

SUMMARY

Under prescribed conditions chloroiridate(IV) and *o*-dianisidine undergo a sequence of reactions resulting in an intense purple colour. This may be made the basis of a photometric determination of iridium in solutions from which the other platinum metals and certain base metals have been removed.

RÉSUMÉ

Dans des conditions déterminées le chloroiridate(IV) et l'*o*-dianisidine donnent une série de réactions qui conduisent finalement à une coloration pourpre intense. Ceci peut constituer la base d'un dosage photométrique de l'iridium après élimination de certains métaux et en particulier de ceux du groupe du platine.

ZUSAMMENFASSUNG

Unter bestimmten Bedingungen geben Chloroiridat(IV) und *o*-Dianisidin eine Reihe von Reaktion die schliesslich zu einer intens purpurroten Farbe führen. Dies kann als Grundlage einer photometrischen Bestimmungsmethode für Iridium dienen, wobei einige Metalle und zwar insbesondere die der Platingruppe entfernt werden müssen.

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CELL CORRECTIONS IN PRECISION COLORIMETRY*

by

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INTRODUCTION

REILLY AND CRAWFORD[1] have pointed out that there are four methods of colorimetry, which differ in the manner in which the instrumental scale is established. Of these methods, the most general and potentially most precise uses two absorbing solutions as references. The equation relating transmittance and concentration in this general case can be reduced to equations describing the other methods. Although YOUNG AND HISKEY[2], BASTIAN[3], and others have devised procedures utilizing one absorbing reference solution, thus far there have been no reports in the literature of the application of the two new methods proposed by REILLY AND CRAWFORD[1]. HISKEY[4], and FREELAND AND FRITZ[5], in application of their methods, considered errors due to variations in cell length. The consideration of variations in the lengths and absorbances of cells becomes critical in the practical application of the methods proposed. Such considerations are discussed in this paper, and methods of correcting for the errors introduced by using unmatched cells are presented.

THEORY

It is generally assumed that the instrumental reading of a photoelectric colorimeter is a linear function of the radiant power issuing from a sample, and can be represented by

$$R = k\ P + k', \qquad \text{(Eq. 1)}$$

where R is the instrumental reading, k is the phototube proportionality constant, k' is the phototube constant, and P is the radiant power received by the phototube.** By using the sensitivity, dark current, and slit controls on the Beckman Model DU spectrophotometer, or analogous controls on other instruments, the following boundary conditions are established:

$$R = \alpha \qquad \text{when } P = P_1$$
$$R = \beta \qquad \text{when } P = P_2.$$

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* Contribution No. 452. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

** The nomenclature used in this paper is that suggested by the committee on Nomenclature in Applied Spectroscopy[6].

The use of these conditions in Eq. 1 permits the values of k and k' to be expressed as

$$k = \left(\frac{\alpha - \beta}{P_1 - P_2}\right),$$

$$k' = \beta - \left(\frac{\alpha - \beta}{P_1 - P_2}\right) P_2,$$

and consequently

$$R = (\alpha - \beta)\left(\frac{P - P_2}{P_1 - P_2}\right) + \beta. \qquad \text{(Eq. 2)}$$

The passage of radiant power through a sample cell is represented in Fig. 1, where

$$\begin{aligned} P_\circ &= P_\circ' \; 10^{A'} \\ P_\circ' &= P' \; 10^{abc} \\ P' &= P \; 10^{A''} \end{aligned}$$

and therefore

$$P = P_\circ 10^{-A} 10^{-abc} \qquad \text{(Eq. 3)}$$

where a is the absorptivity of the absorbing species
b is the internal cell length
c is the concentration of the absorbing species
A is the absorbance of the cell
A' and A'' refer to the absorbances of the individual cell walls.

In the general method outlined by REILLY AND CRAWFORD[1], β is established with a solution of concentration c_2, and α with a solution of concentration c_1 where $c_2 > c_1$.

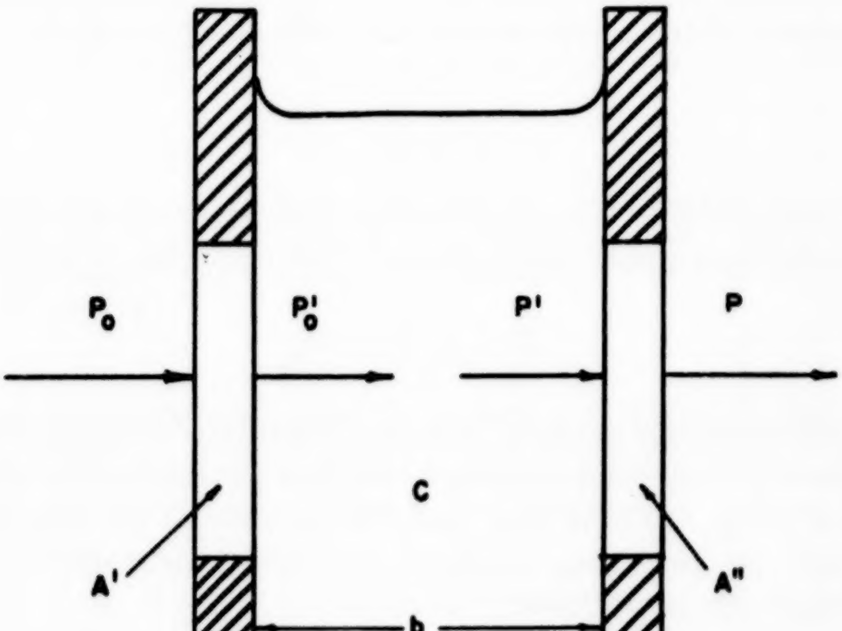

Fig. 1. Cell diagram

Experimentally, this can be done by a series of successive approximations to the correct instrumental settings. In doing this, it is inconvenient to use a single cell because of the necessity of continually rebalancing the instrument. For this reason, and because of the desirability of minimizing the handling of cells, it is recommended that the reference solutions be placed in separate cells, which can be semipermanently positioned in a cell holder.

This method then requires the use of three cells, one for each of the reference solutions, and one for the sample solution. In practice, these cells will not necessarily be matched in absorbance and length.

The subscripts 1 and 2 shall refer to the cells containing reference solutions of concentrations c_1 and c_2 respectively, and the subscript 3 shall refer to the sample cell containing a solution of concentration c_3.

Accordingly we may write an equation for each of the solutions in the several cells as in Eq. 3 as follows:

$$\begin{aligned}
P_1 &= P_\circ \, 10^{-A_1} \, 10^{-ab_1c_1} = q \\
P_2 &= P_\circ \, 10^{-A_2} \, 10^{-ab_2c_2} = r \\
P &= P_\circ \, 10^{-A_3} \, 10^{-ab_3c_3} = x \\
& P_\circ \, 10^{-A_3} \, 10^{-ab_3c_1} = s \\
& P_\circ \, 10^{-A_3} \, 10^{-ab_3c_2} = t.
\end{aligned}$$

The symbols q, r, x, s, t have been introduced for simplicity in the derivations following.

Eq. 2 can now be expressed as

$$R = (\alpha - \beta)\left(\frac{x - r}{q - r}\right) + \beta. \qquad \text{(Eq. 4)}$$

Once having balanced the instrument at α and β with reference solutions of concentrations c_1 and c_2, the observed reading with the solution of concentration c_1 in cell 3 will be α if the cells are matched, and $(\alpha + m)$ if they are not. This can be expressed by the equation

$$R = (\alpha + m) = (\alpha - \beta)\left(\frac{s - r}{q - r}\right) + \beta, \qquad \text{(Eq. 5)}$$

which can be rearranged to

$$m = (\alpha - \beta)\left(\frac{s - q}{q - r}\right). \qquad \text{(Eq. 6)}$$

Similarly, when a solution of concentration c_2 is placed in cell 3, a reading of $(\beta + n)$ is observed instead of β when the cells are not matched.

$$R = (\beta + n) = (\alpha - \beta)\left(\frac{t - r}{q - r}\right) + \beta, \qquad \text{(Eq. 7)}$$

which can be rearranged to

$$r = t - n\left(\frac{q - r}{\alpha - \beta}\right). \qquad \text{(Eq. 8)}$$

Subtracting Eq. 7 from Eq. 6 one can derive

$$(q - r) = \left(\frac{(a - \beta)\ (s - t)}{(a - \beta + m - n)}\right). \qquad \text{(Eq. 9)}$$

Substituting Eqs. 8 and 9 in Eq. 4, one obtains

$$R = (a - \beta + m - n)\left(\frac{x - t}{s - t}\right) + (\beta + n). \qquad \text{(Eq. 10)}$$

If the cells used were matched, such that $b_1 = b_2 = b_3$ and $A_1 = A_2 = A_3$, the observed reading would be equal to (*cf.* Eq. 4)

$$R_T = (a - \beta)\left(\frac{x - t}{s - t}\right) + \beta, \qquad \text{(Eq. 11)}$$

where R_T has been introduced to represent a "true" reading.

The term $\left(\frac{x - t}{s - t}\right)$ appears in both Eqs. 10 and 11. Eliminating this term, one can arrive at the equation

$$R_T = \frac{(a - \beta)\ (R - \beta - n)}{(a - \beta + m - n)} + \beta. \qquad \text{(Eq. 12)}$$

This equation can be plotted as in Fig. 2.

As is customary in normal colorimetry, a calibration curve should be prepared. It is evident from Eq. 11 that a plot of R_T against c_3 will not be linear, and that an appropriate number of solutions of known concentrations are needed for a calibration curve.

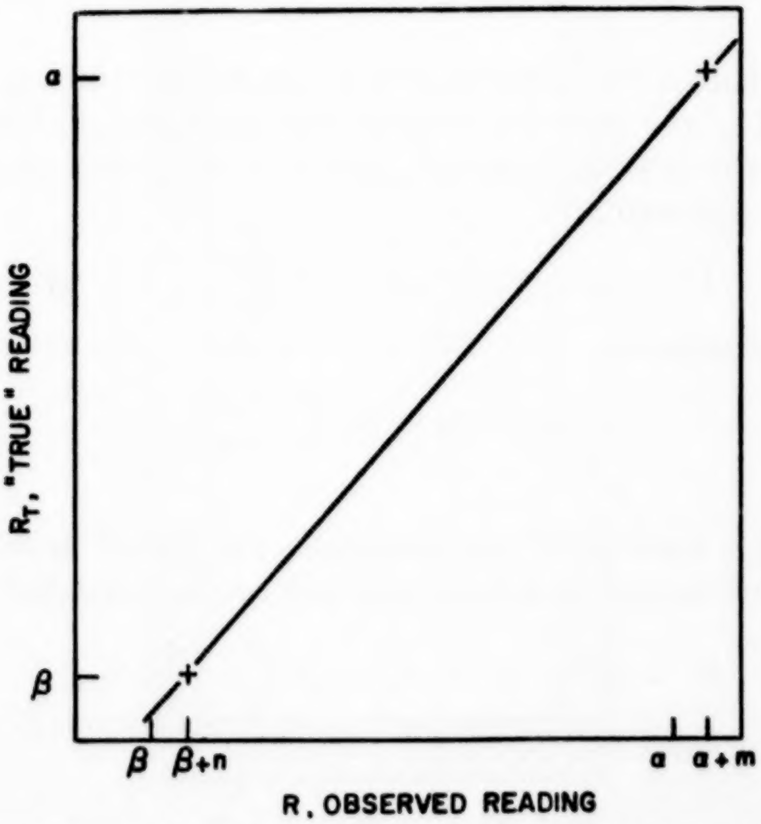

Fig. 2. Suggested graph for correcting the observed reading to a "true" reading.

Method I

In the manner discussed previously, the instrument is balanced, and $(\alpha + m)$ and $(\beta + n)$ are determined experimentally. The readings observed from the measurement of the calibration solutions are corrected to R_T values by means of a graph similar to that in Fig. 2, which may be expanded by means of a folded scale technique. In the same manner, the observed readings of samples may be corrected to R_T values, and the concentration is then read directly from the calibration curve.

As an alternate method, the variations in cell length and absorbances of cells may be compensated for by readjusting the instrument itself. If this is done, the observed reading is, to an approximation, a "true" reading, and can be referred directly to the calibration curve to obtain the concentration.

Method II

As in Method I, the instrument is balanced, and the values of $(\alpha + m)$ and $(\beta + n)$ are determined. The transmittance dial is then set at $(\beta - n)$, after which the instrument is readjusted with the dark current control with the solution of concentration c_2 in cell 2. The solution of concentration c_1 is now placed in cell 1, the transmittance dial is set at $(\alpha - m)$, and the instrument is balanced with the sensitivity control. A sample can then be placed in cell 3, and the reading observed will be R_T.

The validity of this method of compensation can be shown by substituting $(\alpha - m)$ and $(\beta - n)$ for α and β, respectively, in Eq. 4. By substituting Eqs. 8 and 9 into this new expression it can be shown that

$$R = \left[(\alpha - \beta) - \frac{(m - n)^2}{(\alpha - \beta)}\right] \left(\frac{x - t}{s - t}\right) - \left(\frac{m - n}{\alpha - \beta}\right) n + \beta.$$

If $\dfrac{(m - n)^2}{(\alpha - \beta)}$ and $\left(\dfrac{m - n}{\alpha - \beta}\right) n$ are neglected, the equation reduces to Eq. 11. This approximation can be made if the readability of the instrument justifies it. In general, the readability of commercial instruments is never better than ± 0.05% transmission units. It can be shown that this approximation can be made if the conditions

$$(\alpha - \beta)\, dR > (m - n) n,$$

and

$$(\alpha - \beta)\, dR > (m - n) m$$

are met, where dR represents the readability of the instrument.

Method III

Another method may be used which, in effect, employs the same cell for all measurements. A preliminary balancing of the intsrument is made in the manner previously described. The solution of concentration c_2 is then placed in cell 3, and the instrument is adjusted to α with the dark current control. The solution of concentration c_1 is then placed in cell 3 and the sensitivity control is adjusted to a reading of β. The reference solutions in cell 1 and cell 2 are then read and these readings are used to rebalance the instrument throughout the analysis.

DISCUSSION

While all three methods give the same value for the "true" reading there are advantages and disadvantages to each. In Method I the balancing is simpler since the check switch may be used, but new graphs must be prepared frequently. The corrections are made automatically in Method II, but it is not as general since an approximation is made. While Method III is the most straightforward, it requires a stable instrument.

The symbols α and β are used for generality. While α and β are usually 100 and

0 per cent transmission, it may be convient to use other boundary conditions. Such is the case when *n* is negative. However, negative transmittances may be found by extrapolation using the galvanometer deflection. It is always possible to make *n* positive by changing the order of reading the cells.

Although calibration and the application of the methods for correcting for variations in cell length and absorbance will handle some of the errors, it must be kept in mind that there are instrumental limitations, among others, yet to be overcome. A greater sensitivity may be conveniently obtained with a photomultiplier attachment.

Method I has been applied[7] to the analyses of certain rare earth mixtures.

The methods of correction developed in this paper apply to all methods of colorimetry.

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The authors wish to thank Mr. JEROME W. O'LAUGHLIN AND MR. JOHN L. SPOONER for their valuable assistance.

SUMMARY

Errors introduced by the non-uniformity of cells limit the practical application of precision colorimetric theory. The methods of correcting for these errors are not readily evident from the theoretical discussions in recent literature. Three methods of correction for variations in cell length and absorbance are presented.

RÉSUMÉ

Les erreurs introduites par la „non-uniformité" des cuves limitent l'application pratique de la théorie sur la précision colorimétrique. Les méthodes de correction de ces erreurs ne ressortent pas clairement des discussions théoriques dans la littérature récente. Trois méthodes de correction de la variation de longueur et d'absorbance des cellules sont présentées dans ce mémoire.

ZUSAMMENFASSUNG

Die praktische Anwendung der Theorie über die kolorimetrische Genauigkeit wird durch die Fehler begrenzt, welche die fehlende Einheitlichkeit der Zellen mit sich bringt. Aus den theoretischen Diskussionen in der modernen Literatur, sind die Methoden um diese Fehler zu korrigieren, nicht deutlich sichtbar. In der vorliegenden Arbeit werden drei Korrekturmethoden für Variationen der Länge und Absorption der Zellen beschrieben.

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A DIRECT MICROHETEROMETRIC DETERMINATION OF PALLADIUM WITH DIMETHYLGLYOXIME IN EXCESSES OF FOREIGN METALS

by

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INTRODUCTION

The aim of the investigation was to study the heterometric determination of palladium with organic reagents. The results obtained with α-nitroso-β-naphthol have been presented in a special report. A heterometric study of the reaction between palladium and dimethylglyoxime is presented here. The behaviour with both reagents can be summarized as follows: the heterometric determination of palladium with α-nitroso-β-naphthol is about *three* times as sensitive as that with dimethylglyoxime. The error is apparently of the same order of magnitude in each case. In both cases the titration was carried out successfully in the presence of excesses of strong mineral acids and the time taken was approximately the same. Foreign salts, apart from coloured cations, have no influence in either case on the maximum density values as compared with those obtained in the absence of foreign salts. The behaviour towards 50% of alcohol, acetone or dioxan differed in each case: with α-nitroso-β-naphthol the densities increased and the reaction became more sensitive, whilst with dimethylglyoxime the density decreased and the end-point became less sure. In the presence of α-nitroso-β-naphthol large excesses of chlorides acted detrimentally and prevented the precipitation of palladium. No such effect was observed with dimethylglyoxime. The determination with dimethylglyoxime could be carried out successfully in the presence of ⩾ 99% of copper, whilst in similar experiments with α-nitroso-β-napththol no end-point could be obtained and the density rose continuously after the calculated end-point had been reached.

EXPERIMENTAL

Apparatus

The apparatus and the working conditions were the same as in previous investigations [1,*].

The reaction temperature was 20° C. A red filter was used in most cases. In the presence of excesses of foreign coloured salts a safe end-point was generally obtained without the use of a filter (designation: Δ).

In most cases a horizontal density line was obtained after the first maximum optical density point. The end-point was obtained from enlarged curves by the intersection of the line drawn through the density points of the last part of the titration curve with the line drawn through the maximum density points.

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[*] The fundamentals of heterometry are presented in a separate paper[2].

Reagents

All reagents were of analytical grade or chemically pure. The $PdCl_2$ was a pure BDH-reagent and the dimethylglyoxime (= DG) was of analytical grade. An 0.01 M $PdCl_2$ stock solution was prepared by diluting with water acidified with HCl. The concentration of the latter was 0.25 M. More dilute solutions were prepared by dilution of the stock solution with water. The DG was dissolved in distilled alcohol (∼ 95%). The composition of the solutions and the working conditions in special cases are given in the tables.

RESULTS AND DISCUSSION

pH-Heterometric study

A pH-heterometric study was made in order to investigate the pH's at which the palladium is partly or completely precipitated and also the pH's at which palladium remains dissolved. From previous experience in heterometry it is known that the pH of dissolution of a precipitate, once-formed, need not necessarily coincide with the pH at which precipitation occurs. Therefore, the pH of dissolution and of the formation of the precipitate were studied separately. In addition, the titrations were repeated with two different buffer mixtures: one of these contained NH_3/NH_4NO_3, in order to study the influence of *free* ammonia on the palladium-dimethylglyoxime complex (as is well known, Pd(II) forms a very stable complex with NH_3); the second was a borate buffer. The results of these titrations are shown in Figs. 1 and 2. Analysing

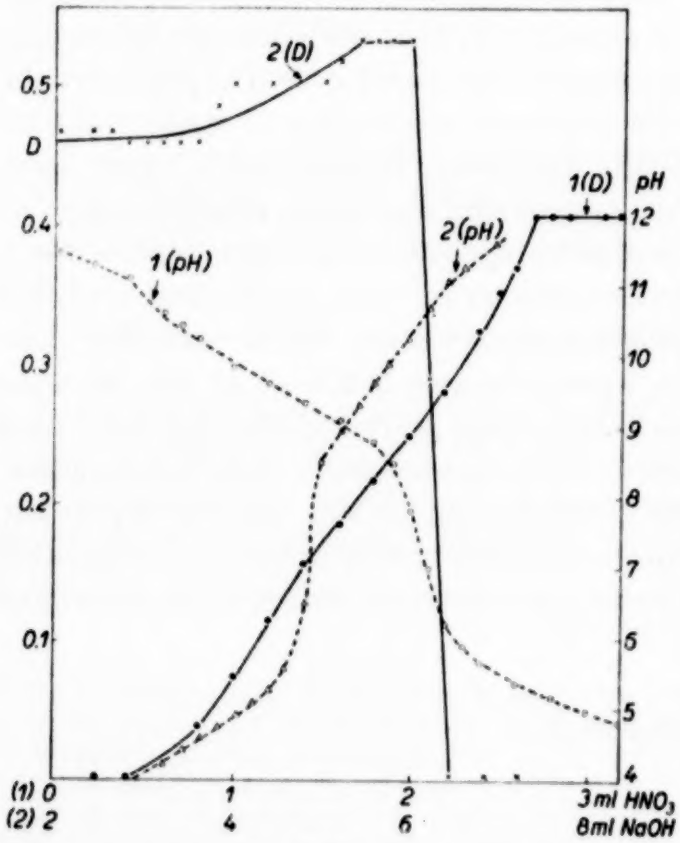

Fig. 1.

1. 2 ml 0.2 M CH_3COOH + 2 ml 0.2 M H_3BO_3 + 7 ml 0.2 M NaOH + 5 ml 0.0033 M $PdCl_2$ (0.08 M HCl) + 3.5 ml 0.01 M dimethylglyoxime (alc.) + 0.5 ml H_2O + x ml 0.2 M HNO_3.
2. 2 ml 0.2 M CH_3COOH + 2 ml 0.2 M H_3BO_3 + 5 ml 0.0033 M $PdCl_2$ (0.08 M HCl) + 3.5 ml 0.01 M dimethylglyoxime + 7.5 ml H_2O + x ml 0.2 M NaOH.

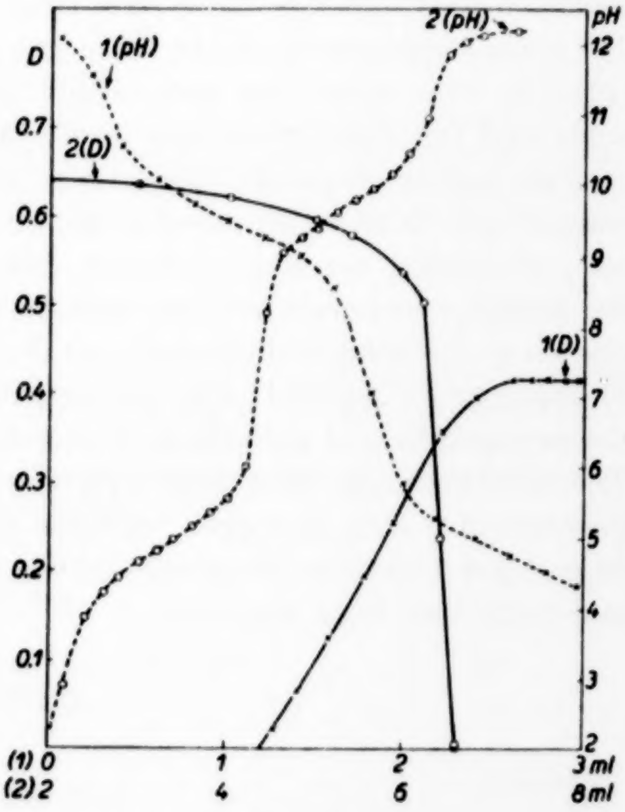

Fig. 2.

1. 2 ml M CH_3COOH + 2 ml M NH_4NO_3 + 5 ml M NaOH + 5 ml 0.0033 M $PdCl_2$ (0.08 M HCl) + 3.5 ml 0.01 M dimethylglyoxime (alc.) + 2.5 ml H_2O + x ml M HNO_3.
2. 2 ml M CH_3COONa + 2 ml M NH_4NO_3 + 3 ml M HNO_3 + 5 ml 0.0033 M $PdCl_2$ (0.08 M HCl) + 3.5 ml 0.01 M dimethylglyoxime + 4.5 ml H_2O + x ml M NaOH.

Fig. 1, the following is found: beginning at a high pH [Fig. 1 curve 1(D)] with a clear solution, the precipitation of $Pd(DG)_2$ begins at pH 11. The amount of precipitate increases almost linearly with decreasing pH values. At pH $\sim$5.2 the precipitation is complete and on decreasing the pH no further influence can be observed.

In the reverse titration, on increasing the pH by the addition of sodium hydroxide [Fig. 1 curve 2(D)] the following is observed: no perceptible dissolution of the precipitate once-formed occurs on increasing the pH's up till pH 10.2, disregarding the fluctuation in the densities. Only on reaching pH 10.2 does a very abrupt linear dissolution occur which is complete at pH 11. Remarkably, there is good agreement between the curves 1 (D) and 2 (D).

It is very interesting to compare the above results with those of Fig. 2 which were obtained using NH_3/NH_4NO_3 buffer. Analysing the curves of Fig. 2, the following is found: beginning at a high pH and decreasing the pH's [curve 1 (D)] the precipitation begins late at pH $\sim$9.3. The amount of precipitate increases almost linearly with decreasing pH's. Quantitative precipitation occurs at about pH 5. In curve 2 (D), (Fig. 2.) the quantitative precipitate which is already formed begins to dissolve at about pH 5. However, the abrupt drop of the density occurs at about pH 11 and a clear solution is rapidly obtained.

Comparing the results obtained with both buffers it may be concluded that although the results of Fig. 1 are more reliable, the differences are slight. It appears that some interference by ammonia is perceptible in Fig. 2, curve 1(D) between pH's 9-11, which may be caused by an ammonia complex of palladium.

Summarizing, it may be said: *quantitative precipitation of Pd(DG)₂ occurs at pH's* $\leqslant$*5. The insoluble complex is completely dissolved at pH's* $\geqslant$ *11. Between these two pH's precipitation is partial.*

TABLE I

Composition: 5 ml 0.0033M $PdCl_2$ (0.08N HCl) + b ml supplements + (15-b) ml H_2O + x ml 0.01M dimethylglyoxime (= DG), alcohol. Temp. = 20° C. Red filter.
Content Pd: 1.78 mg.

Exp. No.	*Supplements*		*DG found ml*	*Initial precip. at ml*	*Max. density value*	*Approx. titration time min.*	*Error %*
1	1 ml	M CH_3COOH	3.10	0.0	0.55	16	0.3
2	1 ,,	M HCl	3.14	0.4	0.54	18	1.6
3	1 ,,	M HNO_3	3.10	0.4	0.58	17	0.3
4	0.5 ,,	M H_2SO_4	3.12	0.0	0.56	15	1.0
5	1 ,,	M CH_3COONa	3.07	0.4	0.59	19	—0.7
6	5 ,,	M CH_3COONa	3.10	0.0	0.60	17	0.3
7	5 ,,	M NH_4Cl	3.16	0.4	0.50	13	2.6
8	5 ,,	M NH_4NO_3	3.05	0.4	0.55	13	—1.3
9	15 ,,	M $(NH_4)_2SO_4$	3.13	0.0	0.63	17	1.3
10	10 ,,	M CH_3OH	3.10	0.6	0.42	16	0.3
11	10 ,,	dioxane	?3.2	0.4	0.31	18	3.6
12	10 ,,	acetone	?3.3	1.4	0.22	28	
13	2 ,,	0.13M $Na_4P_2O_7$	3.07	0.4	0.48	18	—0.7
14	3 ,,	0.1M Na_2-ethylenediamine tetra-acetate		∞	0.0		-
15	3 ,,	0.1M id. + 1 ml M HCl	3.04	0.0	0.73	20	—1.6
16	5 ,,	M Na_3-citrate	3.04	0.4	0.61	21	—1.6
17	5 ,,	M K_2-tartrate	3.15	0.4	0.48	20	1.9

TABLE II

Composition: 5 ml 0.0033M $PdCl_2$ (0.08N HCl) + b ml supplements + (15-b) ml H_2O + x ml 0.01M dimethylglyoxime (= DG), alc. Temp. = 20° C. Red filter. Content Pd: 1.78 mg (or 1.07 mg).

	Content			Found				
Exp. no.	*Supplements*	*Foreign metal mg*	*Pd %*	*DG found ml*	*Initial precip. at ml*	*Maxim. density value*	*Approx. titration time min.*	*Error %*
1	15 ml M $Ca(NO_3)_2$	601.2	0.3	3.13	0.0	0.63	17	+1.3
2	5 ,, ,, $BaCl_2$	686.8	0.3	3.16	0.4	0.52	18	+2.3
3	15 ,, ,, ,,	2060.4	0.1	?3.2	0.2	0.54	20	+3.6
4	15 ,, ,, $MgCl_2$	364.8	0.5	3.18	0.4	0.45	18	+2.9
5	5 ,, ,, $ZnSO_4$	326.9	0.5	3.13	0.4	0.40	18	+1.3
6	5 ,, ,, ,, + 7 ml M Na_3-citrate			3.15	0.4	0.20	15	+1.9
7	5 ,, ,, $MnCl_2$	274.7	0.6	3.12	0.4	0.44	15	+1.0
8	5 ,, ,, ,, + 7 ml M Na_3-citrate			3.12	0.4	0.42	18	+1.0
9	3 ,, ,, $NiCl_2$	176.1	1.0	3.14	0.6	0.52	17	+1.6
10	5 ,, ,, ,,	293.4	0.6	∞	0.8	Δ0.51	16	
11	5 ,, ,, ,, + 1 ml M HCl			3.3	0.4	Δ0.82	28	
12	3 ,, ,, $Co(NO_3)_2$	176.8	1.0	2.98	0.4	0.64	17	—3.6
13	5 ,, ,, ,,	294.7	0.6	3.04	0.4	Δ0.62	2c	—1.6
14	5 ,, ,, ,, + 1 ml M HNO_3			3.10	0.4	0.54	23	+0.3
15	5 ,, ,, ,, + 1 ,, ,, ,,			3.04	0.2	Δ0.53	23	—1.6
16	1 ,, 0.5M $FeCl_3$ + 1 ,, ,, HCl	27.9	6.0	∞	0.2	0.77	28	
17	1 ,, M ,, + 5 ,, ,, Na_3-citrate	55.9	3.0	3.1	0.4	Δ0.42	16	+0.3
18	1 ,, 0.5 ,, ,,	27.9	6.0	3.14	0.4	0.32	19	+1.6
19	1 ,, M $CrCl_3$	52.0	3.3	3.14	0.4	Δ0.55	17	+1.6
20	5 ,, ,, ,,	260.0	0.6	3.15	0.4	Δ0.29	18	+1.9
21	10 ,, ,, $Al_2(SO_4)_3$	539.4	0.3	3.20	0.4	0.57	35	+3.6
22	5 ,, ,, ,, + 10 ml M K_2-tartrate	269.7	0.6	3.10	0.4	0.47	17	+0.3
23	3 ,, ,, $Cu(NO_3)_2$ (with 3 ml $PdCl_2$)	190.6	0.9	1.9	0.4	Δ0.52	17	+2.7
24	5 ,, ,, ,,	317.7	0.6	3.0	0.4	Δ0.69	16	—3.0
25	5 ,, ,, $Cu(NO_3)_2$ + 1 ml M HNO_3			3.0	0.4	Δ0.68	22	—2.9
26	5 ,, ,, ,, (with 3 ml $PdCl_2$)	317.7	0.3	∞∿1.5	0.4	>0.52	13	
27	5 ,, ,, $CdCl_2$	562.05	0.3	3.16	0.4	0.46	16	+2.3
28	5 ,, ,, $Pb(NO_3)_2$	1036.0	0.2	3.18	0.4	0.45	14	+2.9
29	2 ,, 0.5M $Hg(NO_3)_2$	200.5	0.8	3.05	0.4	0.55	23	—1.3

Titrations of palladium with dimethylglyoxime

The results of the titrations are presented in Tables I and II whilst the course of some titrations is given in Fig. 3. The same numeration is used in the tables and the figures.

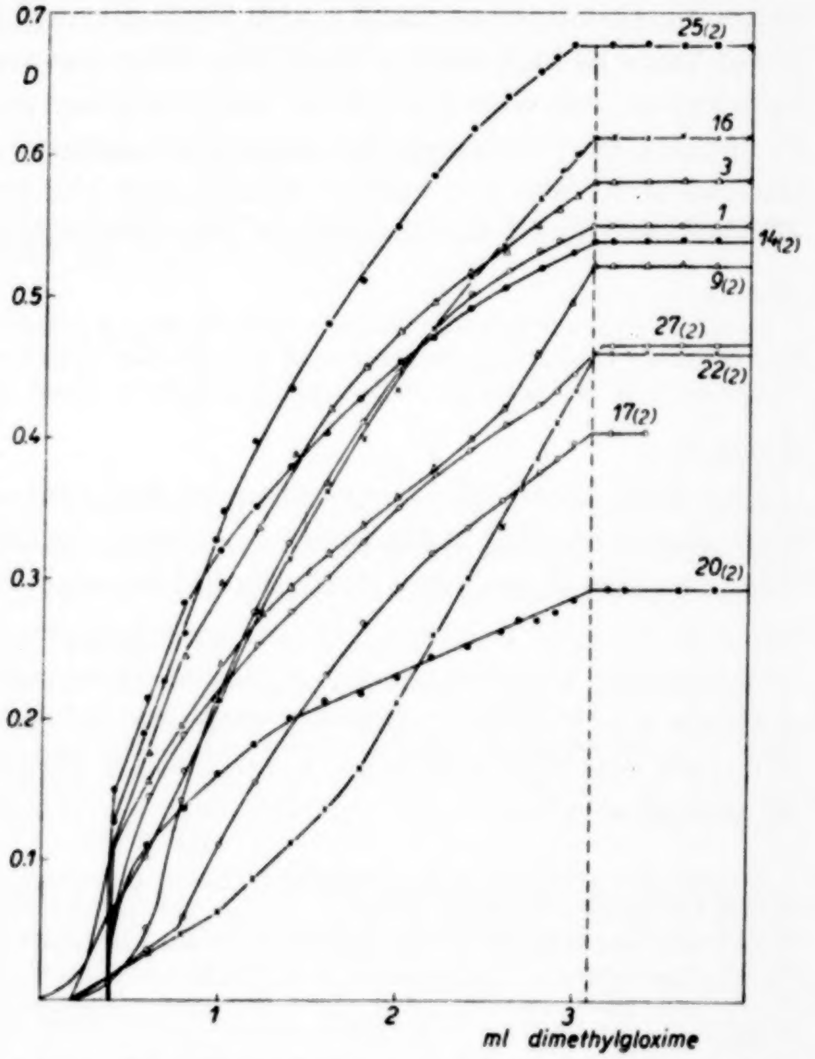

Fig. 3. Titrations of palladium with dimethylglyoxime

In the absence of foreign metals. Table I presents a selection o experiments performed and the results obtained. There is no marked difference in the results, whether acetic acid or mineral acid was added to the (already acidified) solution (exps. 1-4). The presence of large excesses of sodium acetate (exps. 5-6) had no marked influence on the maximum density value. No additional effect was obtained in the presence of excesses of ammonium salts or of mineral acids (exps. 7-9). In 50% acetone or dioxan the maximum density value was greatly depressed and the determination of the end-point was not sure. In 50% methyl-alcohol the maximum density value was also depressed (exps. 10-12). The influence of complexing agents was as follows: pyrophosphate had hardly any influence (exp. 13). No precipitation occurred in solution of Na_2EDTA (exp. 14) but if sufficient HCl was added (exp. 15) the precipitation occurred as usual. Large excesses of Na_3-citrate or K_2-tartrate (exps. 16-17) had no influence whatever. In most cases the error was less than 2%.

In the presence of foreign metals. Table II presents the composition and results of some of the experiments. From the table it can be seen that in no case did the presence of large excesses of foreign metals make the titration impossible. The foreign metal made up > 99% except in the case of iron. In the presence of heavy metals, the foreign metal made up 99.8-99.9% of the total. The palladium could be determined in the presence of the following cations: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Al^{+3}, Fe^{+3}, Cr^{+3}, Pb^{+2}, Cd^{+2}, Cu^{+2} and Hg^{+2}. Masking agents were necessary only in the case of iron. In the presence of copper, higher maximum density values were obtained when no filter was used. In the presence of excesses of coloured cations, parallel titrations were carried out with and without a red filter. Clear end-points were obtained only in the latter case.

Experiments with a deep blue filter

In some investigations carried out in our laboratory it was found that in many heterometric titrations using uncoloured solutions, the maximum density value was about twice as high when a deep blue filter was used. Some experiments which had been carried out with a red filter were therefore repeated using a blue filter instead. It appears that although the maximum density values were about twice as high, the end-point was not certain enough and the errors amounted to 10% or more. The yellow tint of the precipitate was presumably responsible for the deviations.

Method

20 ml of aqueous solution containing 1-1.8 mg of palladium (concentration $5 \cdot 10^{-4}$ — $8 \cdot 10^{-4} M$) and acidified with strong mineral acid, are titrated with a $\sim 0.01 M$ dimethylglyoxime (dissolved in alcohol). A red filter is used. Titration time is about 20 minutes. The error is 0—3%.

Remarks

The table shows the composition of the analysed solution in special cases. No filter should be used in the presence of iron, chromium or copper. In the presence of iron, excesses of sodium citrate should be added.

SUMMARY

Palladium(II) is quantitatively precipitated with dimethylglyoxime at pH's $\leqslant 5$ and is dissolved at pH's $\geqslant 11$. The influence of complexing agents and foreign cations was studied. 1-2 mg palladium in 20 ml aqueous solution, which contained >99% of Ca^{+2}, Ba^{+2}, Mg^{+2}; Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Al^{+3}, Fe^{+3}, Cr^{+3}, Pb^{+2}, Cd^{+2}, Cu^{+2}, and Hg^{+2}, could be determined within 20 minutes with an error of 0—3%.

RÉSUMÉ

Le palladium(II) précipite quantitativement au moyen de la diméthylglyoxime à un pH $\leqslant 5$ et il se redissout lorsque le pH est $\geqslant 11$. Les auteurs ont étudié l'influence des agents complexants et des cations étrangers. Il est possible de doser des teneurs de 1 à 2 mg de palladium dans 20 ml de solution aqueuse, renfermant > 99% de Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Al^{+3}, Fe^{+3}, Cr^{+3}, Pb^{+2}, Cd^{+2}, Cu^{+2} et Hg^{+2}. Le dosage s'effectue en 20 minutes. L'erreur varie de 0 à 3%.

ZUSAMMENFASSUNG

Palladium(II) kann quantitativ mit Dimethylglyoxim bei pH $\leqslant 5$ gefällt werden und geht bei pH $\geqslant 11$ quantitativ in Lösung. Der Einfluss von komplexbildenden Körpern sowie von Fremdmetallen wurde studiert. 1-2 mg Palladium in 20 ml wässriger Lösung die > 99% Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Al^{+3}, Fe^{+3}, Cr^{+3}, Pb^{+2}, Cd^{+2}, Cu^{+2} oder Hg^{+2}, enthielt, wurden innerhalb von 20 Minuten mit einem Fehler von 0—3% bestimmt.

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COMPARISON OF DIFFERENT PALLADIUM-HYDROGEN ELECTRODES AS pH INDICATORS

by

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An investigation of palladium-hydrogen electrodes as indicators of pH has been made because the great absorptive capacity of palladium for hydrogen might permit such electrodes to be substituted for the standard platinum-hydrogen electrodes without the need for bubbling hydrogen over the surface during the measurement. Use of such an electrode would be advantageous, especially for non-aqueous titrations because of its convenience compared to the standard hydrogen electrode and its low resistance compared to the glass electrode. On the other hand, a palladium-hydrogen electrode presumably would suffer from its reactivity with oxidizing agents in the same way as the platinum-hydrogen electrode.

A number of variations in the preparation and use of palladium-hydrogen electrodes have been proposed by previous investigators. For example, palladium black has been deposited upon platinum, gold, and glass as well as upon palladium. Furthermore, although some measurements have been made while passing a stream of hydrogen over the electrode in the usual way, some investigators have fed the hydrogen to the surface through the palladium while others have only pretreated the palladium with hydrogen before immersing the electrode into the solution whose pH was to be determined.

The present study was undertaken to evaluate the conflicting reports in the literature concerning the reliability of the palladium-hydrogen electrodes. In addition, it has indicated sources of deviations of the results. Finally, a promising new design for a palladium-hydrogen electrode has been proposed.

Apparatus and solutions

Most of the measurements in which a glass electrode was used were made with a Beckman Model G pH meter, while measurements involving metal electrodes were made with a Rubicon potentiometer whose scale could be read to the closest 0.5 mv.

Buffer solutions having nominal pH values of 4, 7, and 10, were obtained from Beckman in addition to which five other standard buffers were prepared so that values from approximately pH 2 through pH 10 would be available at intervals of about one pH unit.

Palladium black was deposited from a solution containing 0.5 palladous chloride and 3 ml of 12*M* hydrochloric acid in 50 ml of solution. A deposition current of about 15 ma, passed for 10 minutes, was generally employed.

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TABLE I

COMPARISON OF PH VALUES OF BUFFER SOLUTIONS OBTAINED WITH A GLASS AND A STANDARD HYDROGEN ELECTRODE

Buffer		*Observed pH*	
Number	*Composition*	*Glass*	*Pt-H₂*
1	0.01*M* HCl in 0.1*M* KCl	2.05	2.11
2	Saturated potassium bitartrate	3.57	3.64
3	Beckman "pH 4"	4.02	4.00
4	Phosphate	6.06	6.18
5	Beckman "pH 7"	6.98	7.03
6	Borate — 1	8.05	8.07
7	Borate — 2	9.03	9.07
8	Beckman "pH 10"	9.85	9.97

RESULTS

Preliminary measurements on buffers

A comparison of pH values obtained with the glass electrode with those determined by means of the standard hydrogen electrode, both at 33° C, are shown in Table I. The values in Table I show close agreement between the two electrodes and also between the predicted and experimental slopes for the hydrogen electrode. The average potential of the calomel electrode was calculated from the values for each of the three Beckman buffers to be 220 ± 2 mv.

Palladium black on substances other than palladium

Previous work. BOTTGER[1] noted that when palladium black was deposited upon platinum or gold and a stream of hydrogen was passed over the electrode, the potential was stable for a much longer time than when the regular platinum-platinum black electrode was used. NEWBERRY[2] deposited a thin layer of palladium black onto a glass tube by means of chemical reduction and made electrical contact with the deposit by means of a platinum wire sealed into the glass. Hydrogen was generated by cathodization. After the electrolysis had been stopped, potentials were constant within 0.01 mv, for 15 minutes and within 0.1 mv for 30 minutes. NYLEN[3] using palladium black deposited upon a platinum wire also studied cathodized electrodes but, in addition, successfully substituted prior immersion in 1*M* formic acid for cathodization. The potentials were found to be stable and to give a potential reading accurate to 0.2 mv in buffer solutions.

TABLE II

COMPARISON OF TWO HYDROGEN ELECTRODES

	Potential, mv	
Buffer, No.	*Pt/Pt Black*	*Pt/Pd Black*
3 (pH 4)	464.0	472.5
5 (pH 7)	646.0	648.5
8 (pH 10)	828.0	818.0

Present study. In Table II are shown the results of a brief attempt to repeat the work of BOTTGER using one platinum electrode covered with palladium black and another with platinum black. Using the Beckman buffers of pH 4 and 10 to calculate the slope of the line E' and the intercept $E_{\circ}$, which is also the value of the calomel electrode, we find for the formula

$$E = E_{\circ} + E' \text{pH}$$

values of 221 mv for $E_{\circ}$ and 60.6 (at 30° C) for E' using the standard hydrogen electrode. From these values one can calculate a pH of 7.05 for the "pH 7" buffer.

Comparable calculations made on the palladium black electrode gave the values of 242 mv for $E_{\circ}$, 57.6 for E' and 7.06 for the "pH 7" buffer. If instead of using the actual slope the theoretical slope had been used, the erroneous pH value of 6.72 would have been obtained for the intermediate buffer. This confirms the work of ANDREWS[4] who advised against the use of a palladium-black electrode because it did not follow the thermodynamic slope (and because it appeared to be more sensitive than a platinum electrode to poisons). However, it should be noted that accurate values can be obtained once the actual slope has been determined with known buffers.

Using the procedure of NYLEN, who did not use a stream of hydrogen over the electrode but instead immersed it in 1M formic acid before each determination, values of $E_{\circ} = 189$ mv, $E' = 58.8$ mv (at 30° C) and pH = 7.00 were obtained. These results were found to be very reliable providing the electrode was immersed in formic acid before each measurement and, more important, the solution was not stirred during the measurement.

As one might expect, the sensitivity to stirring was a function of at least two factors: (a) diffusion of sorbed hydrogen from the surface of the electrode and (b) oxidation of the sorbed hydrogen by oxygen dissolved in the solution. Using the buffer of pH 4, a stirring rate of about 300 r.p.m., and a time limit of 3 minutes, it was found that solutions saturated with hydrogen, nitrogen and oxygen changed 2.5 mv, 66 mv, and 600 mv respectively. If we assume that the change which was observed in the presence of nitrogen was due primarily to diffusion of hydrogen from the electrode surface into the solution, the remainder of the change which occurred in the presence of oxygen was due primarily to oxidation. In the absence of agitation, the corresponding changes were 0.0, 0.0 and 45 mv respectively. The substitution of air for oxygen reduced the change in the absence of agitation to 0.5 mv. Hence, under ordinary circumstances, the errors introduced by the presence of air in an unstirred solution would be negligible for most purposes. As one might expect the sensitivity to oxygen increased in alkaline solutions. Thus another set of measurements in stirred solutions showed a change after 3 minutes of 40 mv at pH 4 and at pH 7, but 80 mv at pH 10. Day-to-day discrepancies in the stirring conditions account for the differences found for the pH 4 buffer in the two sets of experiments.

Next, a comparison was made of the two pretreatments, dipping into formic acid and cathodization. The value obtained by cathodization was found not only to be different from that obtained by dipping into formic acid, but also to be less stable. Thus, an electrode treated with formic acid started at 424.5 mv and 10 minutes later read 423.5 mv whereas the cathodized electrode started at 462 mv and read 446 mv 10 minutes later. It would appear, therefore, that this type of electrode is suitable for measurements providing it is pretreated with formic acid and the solution is not stirred during measurement. An empirical calibration curve would, however, be necessary for best results.

A few studies were made using a deposit of palladium black upon a gold wire. The behavior appeared to be quite similar to that reported above for the corresponding platinum electrode so a detailed study of the effects of experimental variables was not made.

Palladium black deposited upon palladium metal

Previous work. In general, electrodes which are used in the absence of a stream of hydrogen (or a solution saturated with hydrogen) should tend to give an unstable potential as a result of diffusion of hydrogen from the palladium black into the aqueous phase and from oxidation of the hydrogen by oxygen (or other oxidants) dissolved in the solution. Hopefully, one might expect that by depositing palladium black upon compact palladium metal a reservoir of hydrogen would be provided which would tend to stabilize the readings of the potential.

BOTTGER[1] did not obtain good results with such an electrode, though NEUMAN[5] had previously been successful and had reported obtaining potentials with the palladium electrodes which were the same as those obtained with the classical hydrogen electrode. Both workers had passed hydrogen over the electrode surface during the measurements. It would appear that NEUMAN had made his electrode with special care and had taken the precaution to wait until the palladium sheet had been saturated with hydrogen before recording his potentials whereas BOTTGER may not have done so. If the palladium had not been saturated, diffusion of hydrogen from the surface layers into the unsaturated portion of the palladium electrode could introduce an appreciable error into the measurement.

Present study. When a palladium-palladium-black electrode was used with a stream of hydrogen in the conventional way, a line with a slope of 58.3 mv was found at 33° C. Though it could be used in the same way as a standard platinum-hydrogen electrode it offered no advantages and, in addition, it required that a calibration curve be made. Though only a limited number of measurements were made, the values appeared to be somewhat less precise than those obtained with a standard hydrogen electrode.

Four different types of precathodized electrodes were tested. Two were spheres 3 mm and 7 mm in diameter; the third was a wire 1 mm in diameter and 2 cm long; and the fourth a sheet 0.13 mm thick and 3 cm^2 in area. In each case the palladium had to be welded to a platinum wire in order to run it through glass because the volume of palladium changed when it absorbed hydrogen and broke the seal. These electrodes were hydrogenated by cathodizing them in 0.1*M* sulfuric acid. After electrolysis, each electrode was washed with distilled water for about 1 minute and then immersed in a buffer solution. The value of the potential depended upon the concentration of hydrogen in the external layer of palladium and was, to a first approximation, a function of the duration and magnitude of the cathodization current.

The potentials of the different electrodes were quite similar but did differ as much as 20 mv from one another. In using them, it was found that they were generally less sensitive to stirring than were the electrodes of NYLEN[3] which consisted of palladium black on platinum. It would seem that in order to diminish the effect of agitation and the resulting loss of hydrogen from the surface layer of the palladium, one should utilize an electrode having a large a ratio of volume to external surface, *i.e.*, large spheres. This would be true if one could saturate the whole sphere with hydrogen without modifying the properties of palladium in an undesirable way. However, an increase in the porosity of the palladium with the time of electrolysis indicated that a time of approximately 30 minutes was optimum when a 30 ma current was employed.

The electrodes were tested by placing them in a stirred buffer solution and measuring the potential as a function of time. At intervals, the stirring was stopped for five minutes and then started again. Fig. 1 shows that the best results were obtained with the wire and sheet (and with the 3 mm sphere which is not shown) whereas the large sphere was distinctly the worst. In each case, the potential decreased with time until agitation was stopped at which point it began to increase. A peak was formed as a result of starting to stir again, thereby making the potential decrease once more. In a sense the height of the peak can be used a measure of the sensitivity of the electrode to agitation. As expected, the sensitivity to agitation of any of these electrodes was approximately 2-5 fold greater at pH 10 than at pH 4. In addition, as shown in Fig. 2, the slopes were greater after a second cathodization, particularly in the case of the 7 mm sphere, thereby indicating an increased sensitivity to stirring. Once again, the changes that occurred with the 3 mm electrode were very similar to those found for the wire. Longer periods of electrolysis produced even greater sensitivity to stirring. In order to restore a palladium electrode to its approximate condition prior to cathodization, it was necessary to heat it over a burner to about 1000° C.

For best results, one can recommend the following conditions. The palladium

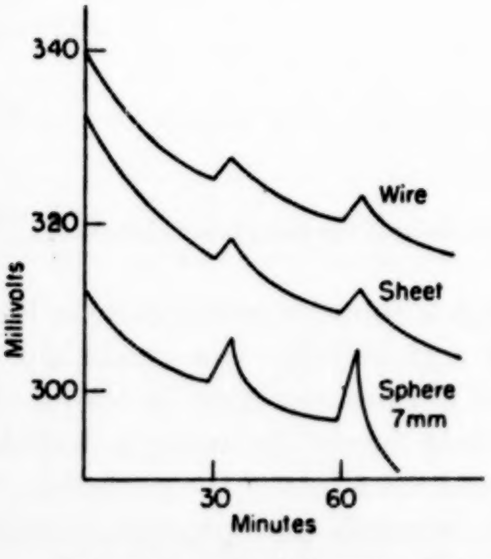

Fig. 1. Behavior of different forms of palladium-palladium black electrodes in a stirred solution of acidic buffer solution after one 30-minute precathodization.

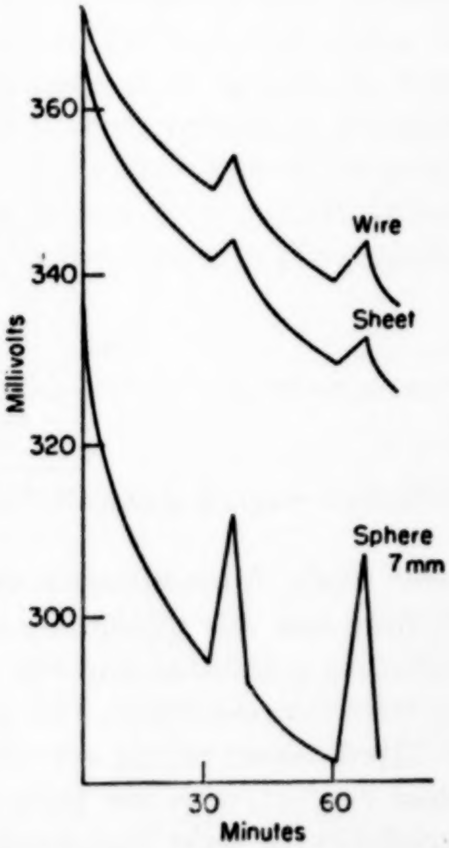

Fig. 2. The effect of a second precathodization of the palladium electrodes without an intermediate ignition step.

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should be thin, preferably of the order of 1 mm in thickness. Pretreatment by cathodizing should take place at a current of about 30 ma for 30 min. Before repeating the cathodization, the electrode should be heated in a flame to restore it to a more compact state. It must be standardized after each cathodization and preferably before each measurement. An electrode can be used for a number of measurements over a three-hour period without need of recathodizing.

Electrodes based upon diffusion of hydrogen through palladium of the electrode surface

Previous work. Wilke[6] employed as an electrode a palladium capillary closed at one end, into which hydrogen was introduced under a pressure of up to 100 atmospheres. However, Kruger[7] in an attempt to use Wilke's electrode found the potentials very difficult to reproduce. Druker[8] approached the problem somewhat differently. He used a 3-electrode system in which one electrode, a palladium foil, was used to divide a U-tube into two portions. One side of the tube contained an electrolyte, such as sulfuric acid, and a platinum electrode. By making the palladium the cathode of this pair it was possible to liberate hydrogen on one side of the electrode. Into the other portion of the U-tube was placed a buffer, whose pH was to be determined, and a reference electrode. The electrolysis and the measurement were carried out alternately by means of an automatic interrupter. The potential difference between the reference electrode and the palladium foil could be used to characterize the pH of the solution. Unfortunately, the nature of Druker's design was such that he could not study the effects of agitation or oxidation of the hydrogen.

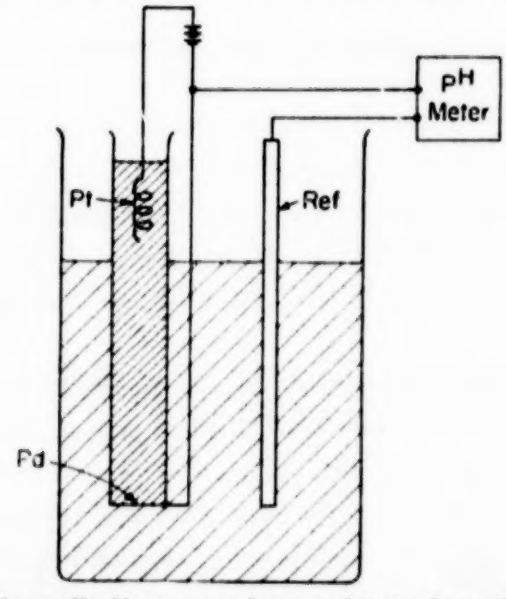

Fig. 3. Schematic diagram of the palladium membrane electrode and the associated electrical circuit.

Present study. A modification of Druker's design is shown schematically in Fig. 3. A palladium foil was mounted across the end of a glass tube. One could dip this electrode into a solution and use it as one would a glass electrode in conjunction with a reference electrode. The palladium was held firmly by using a length of tightly-fitted rubber tubing over the glass tubing and the edges of the palladium foil. Electrical contact with the palladium was made beneath that protective sheath. The possibility of leaks was minimized by coating the end of the glass tube with several layers of rubber glue before the palladium foil was mounted in place and then sealing the outer sheath of rubber tubing with more of the same glue.

Earlier, unsuccessful attempts had been made to use electrodes in which the palladium sheet was simply stuck to the glass using one of a variety of waxes, gums and glues. Expansion of the palladium soon broke the seal in each case. Likewise a design in which the palladium was clamped tightly between two hollow pieces of plastic failed. However, failure in this case appeared to be due to an accumulation of hydrogen bubbles against the lower (indicator) surface of the horizontal palladium sheet and probably could have been eliminated by designing an electrode in which the palladium foil was held in a vertical position.

Using the successful design that was mentioned first, it was possible to study effects of agitation. Furthermore, it was unnecessary to use a commutator as Druker[8] did because measurements could be made without stopping the electrolysis. It is possible to show that the e.m.f. introduced into the measuring circuit could be ignored under the conditions that were employed. Using a current of 20 ma and a resistance of 0.03 ohms the resulting voltage superimposed on the measurement was 0.6 mv. This bias was not only small but also stable because the electrolytic current was quite stable. The use of currents up to 50 ma did not produce significant changes in performance.

Using a palladium sheet 0.13 mm (5 mil) in thickness (coated on both inside and outside with palladium black) and an electrolytic current of 50 ma the potential on the electrode in contact with a Beckman buffer pH of 10 increased, first very rapidly for about 10 min and then more slowly for the next 90 minutes until it reached a value of 805 mv. It remained stable at this value for 5 hours. The next day the experiment was repeated and a stable potential of 810 mv was attained in 30 min. It, too, remained stable for 5 hours. As one might expect, the use of a thinner foil also decreased the time required to reach a stable potential. Thus, after approximately 20 hours of prior electrolysis it was found that a stable potential was reached by a 0.013 mm foil 12 min after being dipped into a solution. The fact that stable values were reached sooner after longer periods of electrolysis is in agreement with the recently published findings of Hoare and Schuldiner[9]. Increased permeability had been reported earlier by Kohler[10], though Kobozew and Monblanova[11], who worked under somewhat different conditions, found that palladium became less permeable. The results of the present study appear to confirm the postulations of Kohler.

TABLE III

SENSITIVITY OF A 0.013 mm PALLADIUM-PALLADIUM BLACK MEMBRANE ELECTRODE TO STIRRING IN DIFFERENT BUFFERS

Buffer No.	*Potential — mv*			*△ pH***
	Pd-Stirring	*Pd-No stirring**	*Std.H_2(Pt)*	
1	381.5	391.5	350.0	0.00
2	472.0	486.0	442.0	+0.04
3	496.0	507.0	464.0	+0.03
4	615.0	633.0	597.0	—0.06
5	675.5	692.5	649.0	+0.07
6	710.0	750.0	712.0	—0.01
7	760.0	810.0	773.0	—0.01
8	836.0	865.0	828.0	0.00

* One minute after stopping the stirrer.

** pH of palladium electrode in unstirred solution, minus that of the standard hydrogen electrode.

As shown in Table III the membrane type of electrode is also sensitive to stirring but much less so than any of the others. In addition, it is interesting to note that the values obtained in unstirred solution produced a slope at 30° C of 60.24 mv per pH unit which is very close to the theoretical value of 60.11. The E_0 value was found to be 264.4 mv. The last column in Table III indicates satisfactory agreement between the pH values determined with the palladium electrode and with the standard hydrogen electrode. In a future study it would be interesting to explore the possibility of decreasing or possibly eliminating the difference in potentials obtained with the palladium and standard hydrogen electrodes by depositing platinum black (or a mixture of palladium and platinum blacks) on a palladium membrane.

An evaluation of the performance of the palladium electrode in an air-saturated buffer solution of pH 6.8 was made using different rates of stirring. As shown in Table IV, slow rates of stirring had relatively little effect on the potential. Approximately the same change was found over the entire acidic range of pH through 7 when a stirring rate of 360 r.p.m. was used. However, at pH values between 8 and 10, the change jumped rapidly to 2-3 times its size at pH 7. Thus deviations between 30 and 50 mv were found in the high pH range.

TABLE IV

EFFECT OF STIRRING RATE ON THE POTENTIAL OF A 0.013 PALLADIUM-PALLADIUM BLACK MEMBRANE ELECTRODE IN A BUFFER OF pH 6.8

r.p.m.	*Potential, mv*
0	639
60	638
120	638
180	634
240	629
300	624
360	619

One electrode worked satisfactorily for over 50 hours before work with it was stopped for other reasons. Though more extended tests are desirable, the electrode in question showed no sign of deterioration. For best results, the values of E' and E_0 should be determined from time to time.

Titrations

In Table V are the results of one set of titrations in aqueous medium of 25 ml portions of sodium hydroxide, containing some sodium carbonate, with 0.1 *M* hydrochloric acid. The results obtained with the palladium membrane, a palladium wire coated with palladium black and pretreated with formic acid, and a glass electrode, agreed with one another and with results obtained using phenolphthalein and methyl orange. The potentiometric curves for all three of the electrodes were similar in shape and had very nearly the same change in potential in the neighborhood of each end-point.

Unfortunately, time did not permit more than a single hurried set of titrations to be made in alcoholic medium some days later. Table V also gives the results of these titrations in which 25 ml portions of sodium hydroxide were added to 75 ml of ethyl alcohol instead of water. The first end-point appeared nearly 2 ml sooner (probably as a result of exposure of the solutions of sodium hydroxide to air) whereas the second end point agreed with the one observed previously. Once again the glass electrode and the palladium membrane electrode produced similar curves as shown in Figure 4. On the other hand, the palladium wire electrode showed an almost steady decrease in potential between 17 and 25 ml. Any small irregularities that appeared on the curve did not seem to be related to the end-point breaks that should have been present.

From the limited number of titrations that were run, it is evident that the palladium membrane electrode will give titration curves in aqueous solutions and in 75% ethyl alcohol which agree very well with the curves obtained with the glass electrode. Although the potentials obtained with the palladium wire electrode have been shown to drift in a stirred solution, the drift was not sufficiently serious in aqueous medium to interfere with the titration curve to a noticeable extent. On the other hand, in an alcoholic medium use of the wire did not appear to be promising on the basis of a single run. Before reaching any definite conclusions regarding the usefulness of either of the palladium electrodes in titrimetry, it is obvious that more extensive studies will be required. It is also obvious that future studies should include work with solutions containing oxidizing agents, both inorganic and organic, in the form of solvents as well as solutes.

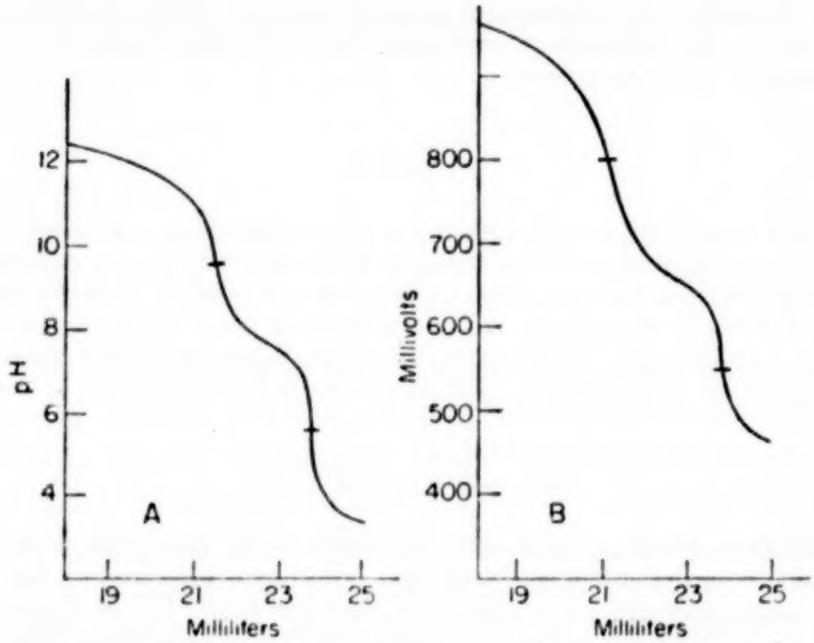

Fig. 4. Titrations of stirred solutions of sodium hydroxide in 75% ethyl alcohol with hydrochloric acid using a glass electrode (A) and a palladium membrane electrode (B).

TABLE V

COMPARISON OF THE END-POINTS OBTAINED IN TITRATIONS OF 25 ml ALIQUOTS OF SODIUM HYDROXIDE (CONTAINING SOME CARBONATE) WITH 0.1 *M* HYDROCHLORIC ACID USING DIFFERENT INDICATORS. SOLUTIONS WERE STIRRED AT 300 r.p.m.

	Indicator	*End-point — ml* *1*	*2*
A. Aqueous			
	Glass	23.20	23.75
	Pd-membrane	23.15	23.60
	Pd-wire*	23.15	23.75
	Visual**	23.20	23.67
B. 75% ethyl alcohol***			
	Glass	21.5	23.7
	Pd-membrane	21.0	23.7
	Pd-wire*	Steady decrease throughout end-point region.	

* Pretreated with formic acid.
** Phenolphthalein (1) and methyl orange (2).
*** Solution of alkali had changed.

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SUMMARY

Different modifications of palladium electrodes have been tested and compared as pH indicators for single measurements and for titrations. The most satisfactory electrode took the form of a palladium membrane on which hydrogen was generated continuously. A simpler type, adequate for many purposes, consisted of a platinum or gold wire on which palladium black has been deposited. The effects on the electrode potential of electrode pretreatment, stirring the solution, and presence of oxygen, were evaluated.

RÉSUMÉ

Différents modèles d'électrodes au palladium ont été examinés et comparés, comme indicateurs de pH pour des mesures simples et pour des titrages. L'électrode la plus satisfaisante est constituée d'une membrane de palladium sur laquelle l'hydrogène est produit continuellement. Un modèle plus simple, suffisant dans de nombreux cas, est constitué d'un fil de platine ou d'or sur lequel du noir de palladium a été déposé. Les auteurs ont étudié également les effets d'un prétraitement de l'électrode, de l'agitation de la solution et de la présence d'oxygène, sur le potentiel d'électrode.

ZUSAMMENFASSUNG

Verschiedene Modelle von Palladiumelektroden wurden als pH-Indikatoren für einzelne Messungen und für Titrationen geprüft und verglichen. Die beste Elektrode besteht aus einer Palladiummembran auf der kontinuierlich Wasserstoff gebildet wird. Ein einfacheres Modell, das für viele Zwecke geeignet ist, besteht aus einem Platin- oder Golddraht auf dem Palladiumschwarz niedergeschlagen ist. Die Einflüsse welche eine Vorbehandlung der Elektrode, Rühren der Lösung und Gegenwart von Sauerstoff auf das Elektrodenpotential ausüben, wurden ermittelt.

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ANODIC POLAROGRAPHY OF SULFUR COMPOUNDS IN PETROLEUM AND ITS FRACTIONS

by

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Differences in the relative ease of oxidation of the sulfur compound types and the recent achievements toward placing anodic polarography at stationary platinum wire electrodes on a sound theoretical basis[3,6] prompted us to apply an anodic polarographic scanning technique to the qualitative examination of crude oils and sulfur concentrates derived from petroleum. Since most polarographs are not equipped with iR drop compensators and the effect of ohmic potential on polarograms obtained with stationary wire electrodes is pronounced[1,7], it was necessary to choose a solvent-electrolyte system with the lowest attainable specific resistance while maintaining high solvent action for petroleum.

The cell resistance was reduced to a minimum by consideration of a number of factors. A search for crude oil solvents having relatively high dielectric constants and good resistivity toward oxidation revealed several organic solvents, of which nitrobenzene appeared to be the best (dissolves crude oil easily and has a dielectric constant of 36.1 at 20° C[2]). The highest possible conductivity was achieved by using an acidic electrolyte, thus taking advantage of the exceptional hydrogen ion conductivity, at the highest practical concentration. By the addition of 30 parts methanol to 70 parts (by volume) nitrobenzene, it was observed that sufficient concentrated hydrochloric acid could be dissolved to produce a $0.2M$ solution without seriously decreasing the solubility of crude oils in the resulting solution. The use of a chloride electrolyte also permitted the utilization of a simplified reference electrode which, in effect, also reduced the cell resistance. A silver electrode, coated with silver chloride, introduced directly into the solvent-electrolyte served as the reference electrode[4,8]. Cell resistances of 250 to 350 ohms were obtained.

Preparation of electrodes and solvent-electrolyte

The platinum wire electrode was prepared by sealing a platinum wire concentrically into a convenient length of soft glass tubing so that about 5 mm of the wire remained exposed. For theoretical work, a small glass bead should be fused to the exposed end of the wire to reduce end effects[6] but this should not be necessary for most qualitative practical applications.

A sturdy silver-silver chloride reference electrode was prepared by sealing a 3 in. length of platinum wire into a convenient length of soft glass tubing leaving the bulk of the wire exposed.

The electrode was plated with silver by electro-deposition from an ammoniacal 2% silver nitrate solution at a current density of about 50 mA/cm^2 for about 1 hour. The deposit tended to be crystalline which thereby increased the effective surface area. The electrode was rinsed in distilled water and anodized, at the same current density, in $1M$ aqueous HCl for about 10 min. This electrode gave reproducible results for days, without repreparation. When repreparation became necessary, the silver was removed in boiling nitric acid and the above procedure repeated. Electrical contact was made through mercury in both of the above electrodes.

The two electrodes were conveniently mounted in a cork so that they were separated by about 5 mm in the solution. A polyethylene gasket was cut to fit between the bottom surface of the cork and the cell. The cell was airtight thus preventing the absorption of moisture which produces convection currents resulting in erratic polarograms.

The solvent-electrolyte was prepared by adding 17 ml of concentrated hydrochloric acid ($12M$) to 300 ml of certified reagent grade methanol (Fisher Scientific Co.) in a 1 liter volumetric flask and diluting to the mark with purified nitrobenzene (J. T. Baker Chemical Co.).

Treatment of the platinum electrode

The treatment of a platinum microelectrode has considerable bearing upon the results obtained[3,5]. NICHOLSON[6] observed that reproducible polarograms could be achieved by pretreating the platinum electrode with an alternating current. Pretreatment was accomplished by connecting the cell to a conductivity bridge (Model RC-1B, Industrial Instruments, Inc., Jersey City, N. J.) operating at 1000 cycles/sec. The pretreatment was applied while the cell came to thermal equilibrium in a constant temperature bath (25.0 ± 0.1° C) for a period of 15 min. Peak currents were reproducible to within 1 or 2%. Without this treatment, wide variations in the peak current were obtained.

TABLE I

DATA TAKEN FROM ANODIC POLAROGRAMS OF REPRESENTATIVE SULFUR COMPOUNDS

Compound	*Decomposition potential*[*] *(volts vs. Ag-AgCl)*	E_{max}[*] *(volts vs. Ag-AgCl)*
2-Thiabutane	0.75	0.87
3-Thiapentane	0.74	0.84
5-Thianonane	0.77	0.90
1-(*p*-Methylphenyl)-1-thiaethane	0.82	0.92
2,6-Dimethyl-4-thiaheptane	0.78	0.91
Thiacyclopentane	0.73	0.83
Thiacyclohexane	0.79	0.87
1,3-Diphenyl-2-thiapropane	0.81	0.92
7-Thiatridecane	0.76	0.89
8-Thiapentadecane	0.77	0.91
Benzothiophene	no wave	
Dibenzothiophene	no wave	
2,5-di-*t*-Octylthiophene	no wave	
1,4-Diphenyl-2,3-dithiabutane	near 1.0	obscured by electrolyte decomposition
5,6-Dithiadecane	near 0.95	obscured by electrolyte decomposition
1-Butanethiol	0.56	no maximum
1-Decanethiol	no wave	
Elemental Sulfur	no wave	
tert-Butyl Trisulfide	no wave	
Hydrogen Sulfide		Gradually increasing current-no defined wave
Acenaphthene		no wave
Naphthalene		no wave

[*] Corrected for ohmic potential and extrapolated to infinite dilution.

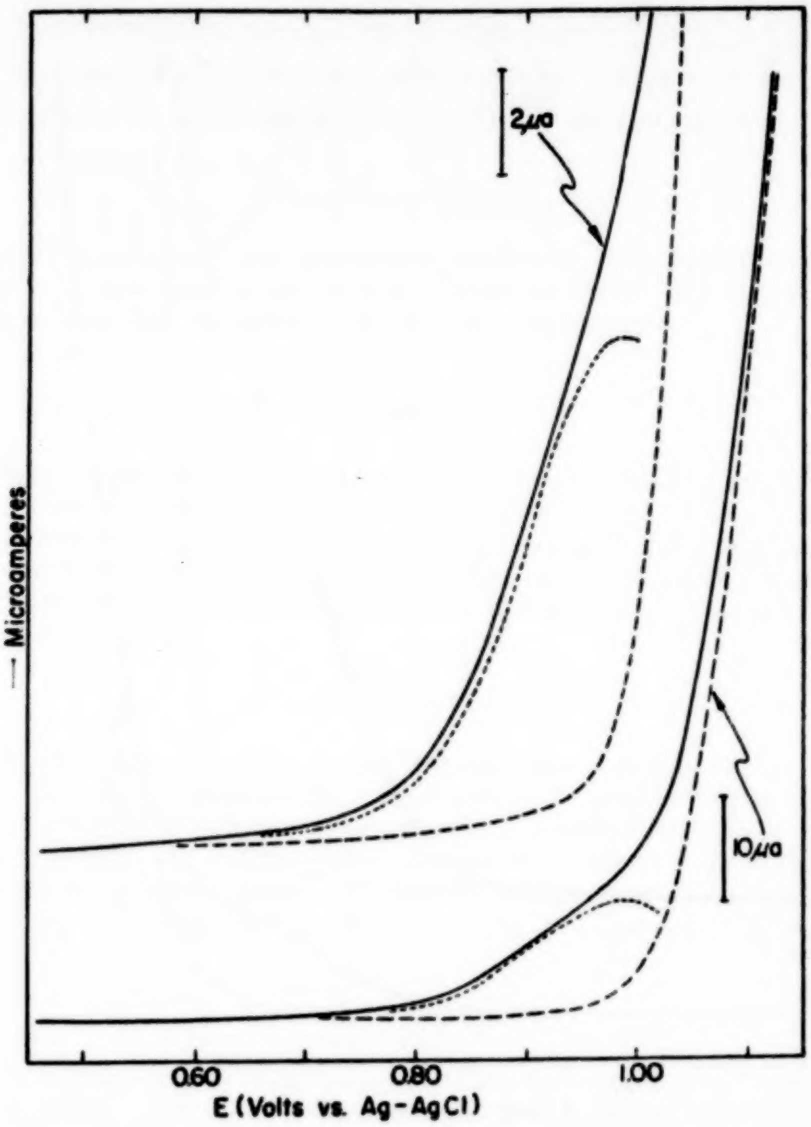

Fig. 1. Anodic polarograms of Santa Maria Valley, Cal., crude oil.
Sample Concn. = 2.909 grams/liter.

———————	Recorded polarogram
— — — — — — — —	Recorded residual current
. . . .	Polarogram corrected for residual current

DISCUSSIONS OF RESULTS

The sulfur compound types which are oxidizable in the usable voltage region of chloride supporting electrolytes are thiols, dialkyl sulfides, cyclic sulfides, and alkyl aryl sulfides. Of the thiols, only those of low molecular weight produced waves. Thiols having molecular weights above about 150 do not yield definite waves but produce polarograms in which the current is only slightly higher than the residual current. For example, *n*-butyl and *iso*-butyl mercaptan exhibit poorly defined waves beginning at about + 0.5 v (*vs.* Ag-AgCl) while *n*-decyl mercaptan does not produce a wave. Hydrogen sulfide behaves like high molecular weight thiols.

In samples such as crude oils and crude oil chromatographic fractions only very low concentrations of thiols, if any, are encountered. Therefore, the only major sulfur types in crude oils which are oxidized by the described procedure are aliphatic sulfides (cyclic and non-cyclic) and alkyl aryl sulfides. Aromatic sulfides, condensed

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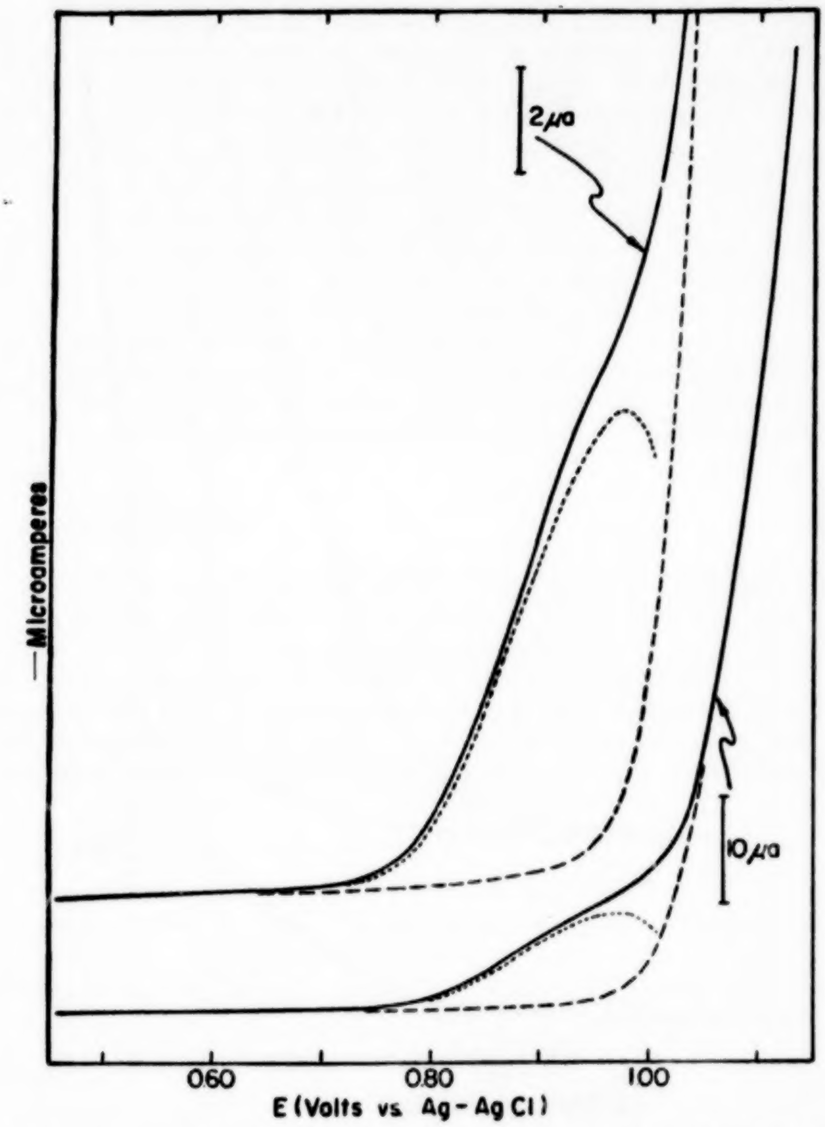

Fig. 2. Anodic polarograms of a chromatographic fraction from North Ward Estes, Texas, crude oil.
Fraction LL-3-2 (3.3% benzene in *n*-pentane eluate from alumina).
Sample concn. = 1.617 grams/liter.
———————— Recorded polarogram
— — — — — — — — Recorded residual current
. . . . Polarogram corrected for residual current

thiophenes, aliphatic and aromatic disulfides, and some polysulfides are oxidized at potentials greater than the decomposition potential of the electrolyte (about + 1.0 v). In conclusion, it should be possible to establish the possible presence of aliphatic and alkyl aryl sulfides from anodic polarograms obtained by the proposed procedure.

Table I presents $E_{\max}$, the potential at which the peak current appears, and the decomposition potential (extrapolation of the straight-line portion of the wave to zero current) of several representative sulfur compounds. Figs. 1 and 2 are anodic polarograms for a crude oil and a crude oil chromatographic fraction, respectively. These polarograms indicate the presence of aliphatic (cyclic and non-cyclic) or alkyl aryl sulfides in the samples.

This technique also has been applied to the semi-quantitative estimation of aliphatic and alkyl aryl sulfide sulfur in sulfur-rich fractions obtained from crude oil. Complete details of this procedure will be published in a subsequent paper.

The preliminary information described in this paper has also been utilized in the development of a controlled-potential electrolytic (coulometric) method for the determination of aliphatic and alkyl aryl sulfides in petroleum.

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SUMMARY

An anodic polarographic procedure is described for the study of sulfur compounds in petroleum. A solvent-electrolyte system containing nitrobenzene has been found which has a high electrical conductivity and in which crude oils are soluble. The preparation and treatment of the platinum electrode is presented whereby polarograms reproducible to 1 or 2% are obtained. Anodic polarograms of crude oils and sulfur concentrates indicate the presence of aliphatic (cyclic and noncyclic) or alkyl aryl sulfides.

RÉSUMÉ

Une méthode polarographique anodique est décrite pour l'étude des composés sulfurés du pétrole. Une solution de base renfermant du nitrobenzène est proposée; elle présente une conductibilité électrique élevée et elle dissout les huiles brutes. La préparation et le traitement de l'électrode de platine sont décrits; on obtient ainsi des polarogrammes reproductibles à 1-2%. Des polarogrammes anodiques d'huiles brutes et de concentrés sulfurés indiquent la présence de sulfures aliphatiques (cycliques et non cycliques) ou de sulfures alkyl-aryl.

ZUSAMMENFASSUNG

Ein anodisches polarographisches Verfahren zur Untersuchung der Schwefelverbindungen im Petroleum wird beschrieben. Ein nitrobenzolhaltiges Lösungsmittel-Elektrolyt-System wurde gefunden, das eine hohe elektrische Leitfähigkeit besitzt und in welchem Rohöle löslich sind. Die Herstellung und Behandlung der Platinelektrode wird beschrieben, mit welcher man bis auf 1 bis 2% reproduzierbare Polarogramme erhält. Anodische Polarogramme von Rohölen und Schwefelkonzentraten weisen auf das Vorhandensein von aliphatischen (cyklischen und nicht cyklischen) oder von Alkyl-Aryl-Sulphiden hin.

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THE POLAROGRAPHIC DETERMINATION OF ELEMENTAL SULFUR IN PETROLEUM AND ITS FRACTIONS

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INTRODUCTION

The processing of crude oils and petroleum fractions containing relatively high concentrations of sulfur compounds has necessitated the development of sensitive, rapid and accurate methods for the determination of sulfur types. Because of the corrosive nature of elemental sulfur, it is important to ascertain accurately its presence, or absence, in crude oil and petroleum products.

Chemical methods for the determination of elemental sulfur were considered too tedious or insufficiently sensitive. HALL[4] applied a polarographic procedure to the determination of elemental sulfur in petroleum fractions using a pyridine-methanol solvent. ECCLESTON, MORRISON AND SMITH[2], modified this procedure by adding benzene to the solvent and applied it to the analysis of crude oils. HALL[5] studied the effect of pH upon the polarograms of elemental sulfur using a benzene-methanol solvent with an acetate-acetic acid buffer system. He proposed procedures for analysis of various sulfur compounds, petroleum fractions and crude oil using this buffered solvent-electrolyte system. Recently, HARRISON AND HARVEY[6] utilized 0.2*M* ammonium acetate in glacial acetic acid for the determination of elemental sulfur in petroleum fractions. This solvent-electrolyte system, however, will not dissolve crude oils.

The procedure described in this paper is a modification of that used by HALL[5]. To insure better solubility of crude oil, the benzene to methanol ratio in the solvent has been increased. Methylene blue has been added as a maximum suppressor to improve the analytical measurement of the wave height. The cumbersome calomel reference electrode was replaced by a silver-silver sulfide anode which is more easily cleaned.

Apparatus

A Leeds and Northrup Electro-Chemograph, Type E, was used throughout. The dropping mercury electrode (Leeds and Northrup Cat. No. 7733-C) had a capillary constant ($m^{2/3} t^{1/6}$) of 1.948 $mg^{2/3} sec^{-1/2}$ for an open circuit with the electrode immersed in the solvent-electrolyte solution described under *Reagents*. The polarographic cell was not thermostated, but room temperature was maintained at 26° C ± 1° C. A single compartment polarizing cell (Leeds and Nortrup Cat. No. 7733-E), designed for use with the mercury pool anode or an external electrode, was employed with a silver-silver sulfide anode as reference electrode. This electrode was prepared by dipping a B & S Gage 22 pure silver wire (several inches in length) into concentrated nitric acid for 2-3 seconds, then without rinsing into a 2% solution of sodium sulfide for 2-3 seconds, followed by rinsing with distilled water. The wire may or may not be sealed into glass tubing. The electrode was reconditioned in the above manner at the beginning of each day.

Reagents

Glacial acetic acid, 99.5%, reagent grade.
Benzene, nitration grade (Jones & Laughlin Steel Corp.)
Methanol, refined (Carbide & Carbon Chemicals Co.)
Methylene blue chloride, total dye content 85% (National Aniline Division)
Sulfur, pure, prepared by method of Bacon and Fanelli[1]
Nitrogen, water pumped (Linde Air Products Co.)
Nitrogen, high purity, dry (Linde Air Products Co.)
Nitrogen, Seaford (Air Reduction Sales Co.)

Solvent-electrolyte solution: In preparing the solvent-electrolyte solution two stock solutions were prepared and then mixed. First, 0.1 gram of methylene blue chloride was dissolved in 100 ml of methanol. Second, 15 grams of ammonium acetate and 5 ml of glacial acetic acid were dissolved in 250 ml of methanol and the solution diluted to 1 liter with benzene. Then 1 ml of the first solution was diluted to 100 ml with the second solution to produce the final solvent-electrolyte, as required. This solution contained 10 mg methylene blue per liter and was 0.19 M in ammonium acetate and 0.087M in acetic acid.

Standards were prepared by dissolving appropriate weighed amounts of pure monoclinic sulfur in benzene using volumetric flasks to produce solutions containing from 0.1 to 1.0 g elemental sulfur per liter. One ml of each of these standards was then diluted to 25 ml with the solvent-electrolyte solution for calibration.

Analytical procedure

The crude oil, or petroleum fraction, was weighed directly into a 25-ml volumetric flask and diluted to the mark with the solvent-electrolyte. Sample sizes were such that the diffusion current did not exceed about 10 microamperes. When the sample dissolved, it was poured into the polarographic cell and degassed for 15 min with prepurified or Seaford nitrogen. The nitrogen was presaturated with solvent-electrolyte vapors, to prevent excessive evaporation of the sample solution, by passing it through a scrubbing bottle containing the solvent-electrolyte. After the degassing period the nitrogen stream was diverted so that the solution was kept blanketed in an atmosphere of nitrogen. A polarogram was then obtained, starting at —0.2 v (*vs.* the $Ag\text{-}Ag_2S$ electrode).

To insure proper functioning of the dropping mercury electrode, after each determination it was immersed consecutively in benzene, methanol, water, concentrated nitric acid, water and methanol, and then dried.

As a result of the high cell resistance (nearly 10,000 ohms) the ohmic potential became large at high elemental sulfur concentrations. A satisfactory wave was obtained if the elemental sulfur concentration in the cell solution was adjusted so that the diffusion current was below 10 microamperes.

The diffusion current, obtained from the height of the wave, was corrected for the residual current and used to calculate the weight percent elemental sulfur from a calibration curve or the equation below:

$$\%\ \text{elemental sulfur} = \frac{(i_d)\ 100}{(k)\ (c)}$$

where i_d is the diffusion current, k is the ratio of $i_{d/c}$ for the elemental sulfur standards, and c is the concentration of the sample in grams/liter.

DISCUSSION OF METHOD

I. Choice of solvent-electrolyte

HALL[4] and ECCLESTON *et al.*[2], used a pyridine-HCl electrolyte and methanol, or a mixture of benzene with methanol, as solvent. When tried in our laboratories, the blank residual currents, using this system, were large and not reproducible throughout a given day. When the benzene to methanol ratio of the solvent was increased, to improve crude oil solubility pronounced maxima resulted.

The sodium acetate-acetic acid electrolyte in 1:1 (by volume) benzene-methanol solvent suggested by HALL[5] gave well-defined polarograms except for pronounced maxima. Substitution of ammonium acetate for sodium acetate produced almost identical polarograms. However, at higher benzene to methanol ratios necessary to dissolve crude oils, ammonium acetate appeared to produce slightly better polarograms than sodium acetate. Also, the solubility of ammonium acetate appeared to be higher than that of sodium acetate in the benzene-methanol solvent mixture. Therefore, ammonium acetate was used in the procedure developed, although sodium acetate may have been satisfactory. For a comparison of elemental sulfur polarograms in various solvent-electrolyte systems, see Figure 1.

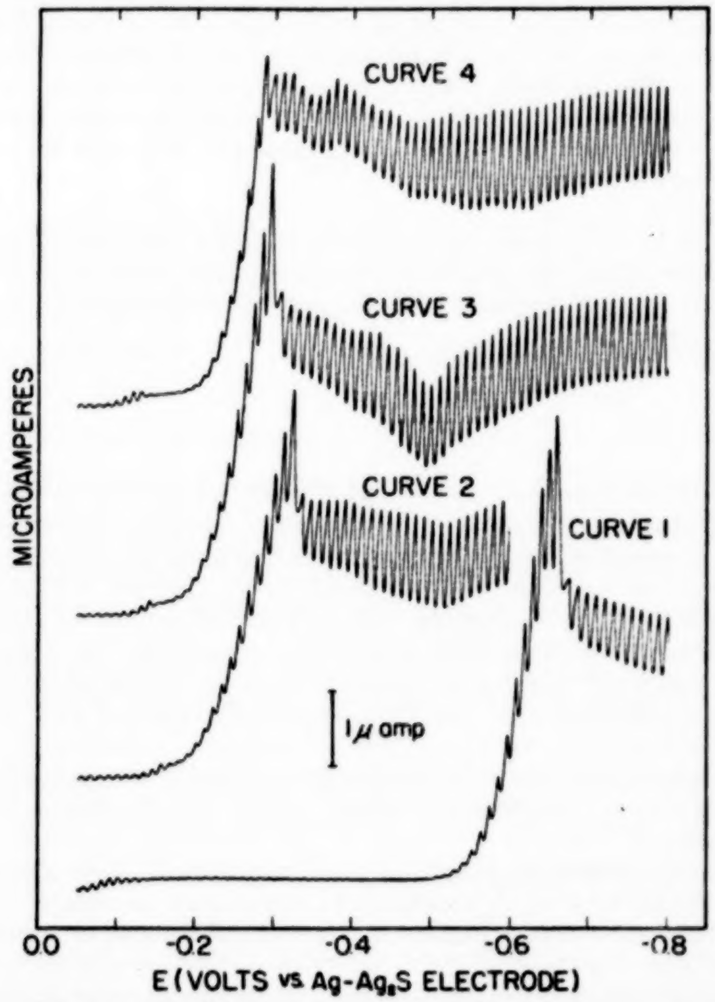

Fig. 1. Nature of elemental sulfur polarograms in various solvent-electrolyte systems, using the silver-silver sulfide anode. Elemental sulfur concentration: 0.00991 g/liter. No maximum suppressor present.

	Solvent-electrolyte composition		
	ml methanol	*ml benzene*	*Other components*
Curve 1	50	50	1.36 g sodium acetate · 3 H_2O, 0.58 ml glacial acetic acid
Curve 2	20	70	9.5 ml pyridine, 0.5 ml conc. HCl
Curve 3	27	63	9.5 ml pyridine, 0.5 ml conc. HCl
Curve 4	45	45	9.5 ml pyridine, 0.5 ml conc. HCl

The polarograms in acetate supporting electrolyte had half-wave potentials (—0.58 v *vs.* Ag-Ag_2S electrode) which were about 0.3 v more negative than in the pyridine-HCl electrolyte (—0.25 v *vs.* Ag-Ag_2S electrode). This separated the elemental sulfur wave from a very small unexplained pre-wave (see Figure 1) which appears in both the pyridine-HCl and the acetate supporting electrolytes at —0.10 to —0.15 v (*vs.* Ag-Ag_2S electrode). Between —0.15 v and —0.45 v (*vs.* Ag-Ag_2S electrode) the polarograms in acetate media exhibited low residual currents, a desirable feature for analytical work.

II. Choice of anode

HALL[4,5] and ECCLESTON *et al.*[2]. used a saturated calomel electrode. The fritted disk separating the saturated calomel half-cell from the dropping mercury half-cell was difficult to keep clean. A mercury pool anode was tried, but the discoloration of the surface through reaction with elemental sulfur in the cell solution and the poor blank residual currents obtained led to its being discarded. A silver-silver sulfide electrode gave results similar to those obtained with the saturated calomel electrode, except that the half-wave potentials were nearly 0.2 v less negative. Since it was considerably more convenient and the polarograms obtained were more reproducible, the silver-silver electrode was chosen for the analytical procedure.

III. Effect of methylene blue concentration

The effects of methylene blue as a maximum suppressor was studied over the concentration range 0.1 to 80 mg/liter (Figure 2). In order to eliminate all evidence of a maximum in the elemental sulfur wave, using the procedure developed, it was necessary that the methylene blue concentration be at least 5 mg/liter (of cell solution). The reduction of methylene blue ($E_{1/2}$ near —0.15 v *vs.* Ag-Ag_2S), when present in high concentration, makes the measurement of small diffusion currents difficult. A methylene blue concentration of 10 mg/liter (actually as methylene blue chloride) was arbitrarily selected.

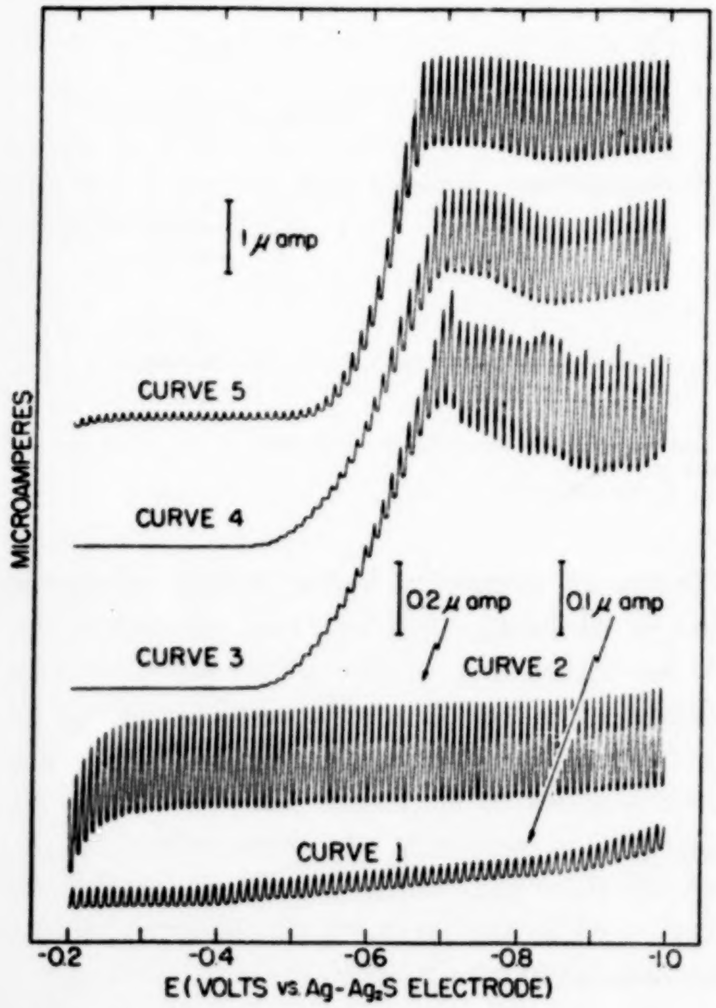

Fig. 2. Effect of methylene blue concentration. Solvent-electrolyte composition given in procedure. Elemental sulfur concentration: 0.01427 g/liter.

	Methylene blue Concentration (mg/liter)
Curve 1 — residual current curve	10
Curve 2 — residual current curve	80
Curve 3 — elemental sulfur	0.10
Curve 4 — elemental sulfur	10
Curve 5 — elemental sulfur	80

IV. Effect of pH

To determine the effect of pH, five different solutions were prepared. Fifteen grams of ammonium acetate and 5 ml of ammonium hydroxide or 0, 5, 10, or 15 ml of glacial acetic acid, respectively, were dissolved in 250 ml of methanol, 10 ml of methylene blue solution (1 mg/ml in methanol) added and the solutions diluted to 1 liter with benzene. The "apparent pH" values of the solutions, as measured with the glass-saturated calomel electrode system, were 8.63, 7.82, 7.27, 7.00 and 6.75, respectively. No significant differences in the diffusion currents or the half wave potentials for a given elemental sulfur concentration in these different solvent-electrolyte systems was noted.

V. Removal of dissolved oxygen — effect of nitrogen purity and degassing time

Because of polarographic interference of molecular oxygen, and its greater solubility in nonaqueous solvents, its removal is of greatest importance. For this reason pyridine, which is known to form strong complexes with halogens and probably also with oxygen[3] has been eliminated from the solvent-electrolyte used.

A number of different grades of nitrogen were examined to determine whether some could be used without further purification. It can be concluded from Table I that either high purity (dry) or Seaford nitrogen may be used directly and that the degassing time need only be 15 min.

The necessity for blanketing the solution with nitrogen while the polarogram is being recorded cannot be overemphasized.

TABLE I

EFFECT OF DEGASSING TIME AND GRADE OF NITROGEN USED ON RESIDUAL CURRENT

Degassing time min	*Microamperes between —0.20 v and —0.80 v*		
	Water pumped nitrogen	*High purity, dry nitrogen*	*Seaford nitrogen*
5	0.54	0.12	0.074
10	0.37	0.073	0.065
15	0.27	0.078	0.056

VI. Reproducibility and accuracy

Except for samples containing only traces of elemental sulfur, where optimum sample weights could not be taken because of solubility considerations, the procedure yielded results which were reproducible to within 1% of the sulfur present. The accuracy of the method for samples of crude oil or petroleum fractions could not be established because of the uncertainty of possible effects of other sulfur types, especially polysulfides. However, study of a series of synthetic samples (Table II) shows an accuracy generally better than 5% in recovery of added sulfur. It is extremely interesting that the recovery of elemental sulfur added to crude oils containing elemental sulfur was quantitative while the recovery of elemental sulfur added to crude oils containing no sulfur was only about 96%.

TABLE II

RECOVERY OF ELEMENTAL SULFUR ADDED TO CRUDE OILS

Sample	*Percent elemental sulfur*		*Percent recovery*
	Added	*Found*	
Butler County, Pa.	None	None	—
(15.94 g crude/liter	0.0293	0.0280	95.6
of solvent-electrolyte)	0.0586	0.0556	94.9
	0.1465	0.1402	95.7
Light Mara, Venezuela	None	None	—
(8.253 g crude/liter	0.0550	0.0538	97.8
of solvent-electrolyte)	0.1100	0.1075	97.7
	0.275	0.264	96.0
Kuwait	None	None	—
(9.033 g crude/liter	0.0504	0.0490	97.2
of solvent-electrolyte)	0.1008	0.0977	96.9
	0.252	0.240	95.2
McElroy Field, West Texas	None	0.338	—
(0.7129 g crude/liter	0.609	0.952	100.8
of solvent-electrolyte)	1.031	1.383	101.4
	1.217	1.556	100.1
	2.062	2.407	100.3
West Texas, Current	None	0.0792	—
Receipts, Port Arthur Refinery	0.1186	0.1975	99.7
(3.656 g crude/liter	0.2010	0.2845	102.1
of solvent-electrolyte)	0.2373	0.3186	100.9
	0.4020	0.4811	100.0

VII. Analysis of samples

Ten crude oil samples, 1 sample of catalytic charge stock and an API elemental sulfur standard were analysed by the proposed method by two different laboratories (Mellon Institute and Gulf Research and Development Company). The results are presented in Table III.

TABLE III

RESULTS OF THE ANALYSIS OF SOME TYPICAL SAMPLES FOR ELEMENTAL SULFUR

Sample	*Percent elemental sulfur*	
	Gulf Research and Development Co.	*Mellon Institute*
Crude MB (Stettler)	0.0055 ± 0.0001	0.0048 ± 0.0002
Crude MC (Stettler)	0.0042 ± 0.0000	0.0036 ± 0.0001
Crude MO (Stettler)	0.0053 ± 0.0001	0.0052 ± 0.0002
Crude LJ (Canada)	nil	nil
Crude NR (Kuwait)	nil	nil
Crude NW (West Texas)	0.352 ± 0.002	0.332 ± 0.001
Crude NV (West Texas)	0.0877 ± 0.0004	0.086 ± 0.001
P-34-281c Catalytic Charge Stock	nil	nil
API-COAR* Sample A	0.095 ± 0.001	0.094 ± 0.001
Crude A	0.521 ± 0.004	0.525 ± 0.004
Crude B	0.900 ± 0.001	0.852 ± 0.004
Crude C	0.480 ± 0.005	0.469 ± 0.004

* American Petroleum Institute, Division of Refining, Committee on Analytical Research.

ACKNOWLEDGEMENT

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SUMMARY

An improved procedure for the polarographic determination of elemental sulfur in crude petroleum is described. Acetic acid and ammonium acetate dissolved in a 3 : 1 (by volume) mixture of benzene and methanol is used as the solvent-electrolyte. Methylene blue is utilized as a maximum suppressor and a silver-silver sulfide anode immersed in the cell solution is substituted for the cumbersome saturated calomel electrode. Reproducibility of the method is about 1% and the accuracy is estimated to be better than 5%, relative.

RÉSUMÉ

Une méthode perfectionnée est décrite pour le dosage polarographique du soufre élémentaire dans un pétrole brut. On utilise comme solution de base une solution d'acide acétique et d'acétate d'ammonium dans un mélange benzène-méthanol, 3 : 1 (en volume). Le bleu de méthylène est employé pour supprimer les maxima. Une anode argent-sulfure d'argent, plongée dans la solution, remplace l'encombrante électrode au calomel saturée. La reproductibilité de la méthode est environ de 1% et la précision relative est meilleure que 5%.

ZUSAMMENFASSUNG

Ein verbessertes Verfahren zur Bestimmung von elementarem Schwefel in Rohpetroleum wird beschrieben. Eine Lösung von Essigsäure und Ammoniumacetat in einem Gemisch von Benzol und Methanol im Volumverhältnis 3 : 1 wird als Lösungsmittel-Elektrolyt-System verwendet. Methylenblau dient zur Unterdrückung der Maxima. Eine in die Lösung eingetauchte Silber-Silbersulphid-Elektrode ersetzt die gesättigte Calomel-Elektrode. Die Reproduzierbarkeit der Methode ist ungefähr 1% und die relative Genauigkeit ist höher als 5%.

REFERENCES

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BOOK REVIEW

The basic principles for pharmacopoeial tests, par F. Reimers, Heinemann, Medical Books, Ltd., London, 1956, 113 p.

This treatise is concerned with the guiding principles in preparing a pharmacopeia. It discusses the problems of identification and the control of the purity of substances in this field. The test reactions are of the classical type and can be performed with a minimum of simple apparatus. Some elementary methods for the determination of physical constants are discussed, as well as methods for quantitative determinations in drugs. Some micromethods are briefly mentioned.

The booklet poses many questions, and can be helpful in indicating solutions of problems and inspiring the reader to find a solution.

H. A. J. Pieters (Geleen)

DETERMINATION OF CARBON-TYPE COMPOSITION AND MOLECULAR WEIGHT OF MINERAL OIL FRACTIONS FROM VISCOSITY, REFRACTIVE INDEX AND DENSITY BY MEANS OF NOMOGRAMS

by

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INTRODUCTION

Recently[1] a method has been described to determine the carbon-type composition* of mineral oil fractions from the physical constants viscosity**, refractive index and density. These constants were the coordinates in a three dimensional figure. Cross-sections for constant log ν_{20} values were made. The intersections of these constant log ν_{20} planes with the surfaces of equal values of $\%C_A$ and $\%C_N$ gave practically straight lines. These straight lines represented equal values of $\%C_A$ and $\%C_N$ respectively.

As these lines in the cross-sections are practically straight it is possible to represent these lines by points in a system consisting of parallel coordinates (nomograms). The different lines in the cross-sections are represented by different points in the nomograms. If the lines in the cross-sections are running parallel*** then the points in the nomogram constitute a straight line parallel to both coordinates.

DESCRIPTION OF THE NOMOGRAMS

In the figures 1 to 6 nomograms have been given which replace the analogous cross-sections for constant log ν_{20} values of the log ν-n-d space model formerly discussed[1].

These nomograms make it possible to construct several quantities at once. These quantities may be structural elements or physical constants, if only the quantities constitute straight lines for equal values of them in the sections.

From the different structural elements and physical constants in this article are chosen the average molecular weight, $\%C_A$ and $\%C_N$. Other quantities will be discussed in other papers.

The given nomograms are easy to handle. To illustrate their use the following example is given.

Of fraction 5 of tin 5 (Rumania oil) the following constants are known:

$$\log \nu_{20}^{cs} = 0.828$$

$$n_D^{20} = 1.4695$$

$$d_4^{20} = 0.8390$$

n_D^{20} = refractive index for the sodium D-line at 20°C.

ν_{20}^{cs} = viscosity in centistokes at 20°C.

d_4^{20} = density at 20°C in g per ml.

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* Viz. $\%C_A$ = percentage of carbon present in aromatic rings, $\%C_N$ = percentage of carbon present in naphthenic rings.

** In this paper revised values for the viscosities have been used, the reason being that the accuracy of the viscosity measurements has been increased recently. Generally the differences are not large.

*** This was true for practically all the lines for equal $\%C_A$ and $\%C_N$.

TABLE

Fraction		$\log \nu_{20}^{cs}$	$\log \nu_{20} = 0.300$			$\log \nu_{20} = 0.500$			$\log \nu_{20} = 1.000$			$\log \nu_{20} = 1.500$		
			$\%C_A$	$\%C_N$	M	$\%C_A$	$\%C_N$	M	$\%C_A$	$\%C_N$	M	$\%C_A$	$\%C_N$	M
Tin 1 VENEZUELA														
fr.	1	0.319	11.5	31	169	8	26	197						
	2	0.455	14	33	168	11	28	195						
	3	0.602				13	29	192	8	19	268			
	4	0.752				15	30	191	10	19	263			
	5	0.953				17	32	189	11	22	258			
	6	1.129							13	25	250	9	15	366
	7	1.334							15	28	244	11	19	350
Tin 2 BORNEO														
fr.	1	0.324	8	56	161	4	48	185						
	2	0.390	12	58	160	8	50	183						
	3	0.473	16	61	158	12.5	52	180						
	4	0.543				17.5	51	179	12.5	43	230			
	5	0.622				22	51	177	17	42	227			
	6	0.709				27	50	176	22	40	224			
	7	0.816				31	50	175	26	40	220			
	8	0.911				37	47	175	31	35	219			
	9	1.100							33	37	216	31	35	253
Tin 3 MEXICO														
fr.	1	0.311	7	30	170	4	25	200						
	2	0.435	11	35	168	8	28.5	196						
	3	0.624				12.5	34	189	7	25	260			
	4	0.871				17	39	185	12.5	29	246			
	5	1.158							16	35	235	12	27	323
	6	1.546										16	33	291
	7	1.977										20	37	274
	8	2.445												
Tin 4 BORNEO														
fr.	1	0.242	23	28	167	20	22	194						
	2	0.299	25	29	166									
	3	0.358	28	30	165	25	24	189						
	4	0.428	32	30	164	29	24	187						
	5	0.489	34	31	162	32	25	186						
	6	0.556				33	26	184	28	11	242			
	7	0.634				35	26	184	29	11	240			
	11	1.187							27	17	237	23	11	319
	12	1.506										26	16	294
Tin 5 RUMANIA														
fr.	1	0.254	8	27	171	5.5	19	203						
	2	0.365	11	29	170	8.5	23	199						
	4	0.649				15	27	193	10	15	268			
	5	0.828				17	29	191	12	18	262			
	6	1.033							13	22	255	9	12	376
	7	1.257							16	25	246	11	15	355
	8	1.507										15	20	333

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* The correction for the presence of sulphur amounts to 3% C_N for each percentage of sulphur a
it is the same for all three methods mentioned in the table (nomogram, space-model, n-d-M metho
No correction was to be applied to $\%C_A$ and M.

ART 1

log ν_{20} = *2.000*			*log* ν_{20} = *2.500*			*Nomogram*			*Space-model*		*n-d-M-method*		M_{exp}	*Corr* for S*
$\%C_A$	$\%C_N$	*M*	$\%C_A$	$\%C_N$	*M*	$\%C_A$	$\%C_N$	*M*	$\%C_A$	$\%C_N$	$\%C_A$	$\%C_N$		
						11	31	172	10	30	12	34	164	
						12	29	189	12	28	13	31	181	
						12	27	208	12	26	13	27	203	
						12.5	23.5	227	13	24	13	24	224	—1
						12	22	252	13	23	12	23	261	—1
						12	20.5	280	11	21	13	22	277	—2
						12	20	308	12	19	13	21	303	—2
						7.5	55	164	7	55	5	56	176	
						10	54	170	10	55	9	55	177	
						13	54	177	13	52	12	55	180	
						17	50	183	18	51	17	50	184	
						21	49	189	21	48	21	47	190	
						25	46	196	25	44	24	43	198	
						28	44	203	28	42	27	40	209	
						32	37	211	32	35	31	35	214	
						33	37	223	32	36	33	35	227	
						7	29	172	7	30	7	30	176	—1
						9	30	187	9	29	8	30	194	—1
						11	31	207	12	30	11	31	213	—1
						14	30	230	14	29	14	28	243	—2
						15	29	263	15	28	15	28	269	—3
15	27	389				16	28	300	16	29	16	27	308	—4
18	31	348				18	26	345	18	25	17	26	355	—5
21	34	321	19	29	409	19	25	399	20	27	19	24	396	—5
						24	30	159	23	30	26	30	152	
						25	29	166	25	28	27	29	159	
						27	28	172	28	26.5	28	29	166	
						30	26	179	30	25	31	28	169	
						32	25	185	32	24	32	28	175	
						32	24	190	33	24	33	23	181	
						33	22	199	33	21	33	22	188	
						25.5	15	268	26	16	25	16	272	
						26	16	295	26	17	25	16	313	
						9	29	164	9	30	11	30	158	
						10	27	179	11	27	12	29	172	
						14	23	215	14	23	15	24	208	
						14	22	238	14	22	15	22	232	
						13	21	262	13	22	14	23	264	
						13	20	302	14	20	14	22	291	
						15	19	335	15	19	15	19	339	—1

TABLE

Fraction	$\log \nu_{20}^{cs}$	$\log \nu_{20} = 0.300$			$\log \nu_{20} = 0.500$			$\log \nu_{20} = 1.00$			$\log \nu_{20} = 1.500$		
		$\%C_A$	$\%C_N$	M	$\%C_A$	$\%C_N$	M	$\%C_A$	$\%C_N$	M	$\%C_A$	$\%C_N$	M
Tin 6 SUMATRA													
fr. 1	0.160	9	30	170	6	25	200						
2	0.196	10	31	169	7	26	198						
3	0.252	11	33	168	8	27	196						
4	0.312	13	35	167	10	29	194						
5	0.378	15	36	166	12.5	30	192						
6	0.447	17.5	38	165	16	32	190						
7	0.529				17	34	188	12	23	256			
8	0.613				19	35	187	14	25	250			
9	0.713				21	36	185	16	25	246			
10	0.840				22.5	38	184	18	27	241			
11	1.010							20	28	237			
12	1.244							23	31	230	19	25	302
13	1.644										25	28	276
Tin 7 SUMATRA													
fr. 1	0.228	13	22	171	11	15	203						
2	0.283	15	23	170	12.5	16	201						
3	0.356	18	24	169	15	17	198						
4	0.419	21	26	168	18	19	196						
5	0.493				19.5	21	194						
6	0.575				21	22	192	16	11	266			
7	0.663				21	23	192	16	12	265			
8	0.765				19.5	25	192	15	12	265			
9	0.853				18	25	192	14	14	265			
10	1.009							13	15	263			
12	1.348							15	21	253	10	12	371
13	1.647										12.5	17	345
Tin 8 VENEZUELA													
fr. 1	0.423	14	46	163	10	39	188						
2	0.806				20	48	180	15	39	232			
3	1.309							22	44	221	18	38	275
4	1.974										24	43	255
5	2.687												
Tin 9 TEXAS													
fr. 1	0.260	7	25	172	5	17	205						
2	0.363	9.5	29	170	6.5	22	200						
3	0.474	13	31	169	10	25	197						
4	0.604				14	28	193	9	18	269			
5	0.772				16	32	189	11	22	258			
6	0.960				19.5	36	186	15	25	248			
7	1.183							18	29	240	14	20	335
8	1.450							21	31	232	17	25	310
11	2.609												
Tin 11 TEXAS													
fr. 1	0.274	9	29	170	6	23	200						
2	0.367	12	31	168	9	25	197						
3	0.488	16	33	167	13	27	194						
4	0.643				16	29	191	11	17	263			
5	0.818				19	32	188	14	21	256			
6	1.032							15.5	25	248	11	15	359
7	1.274							18	28	241	14	19	338
8	1.549										16	23	319
9	1.887										18	28	298
10	2.283												

---

* The correction for the presence of sulphur amounts to 3% C_N for each percentage of sulphur an is the same for all three methods mentioned in the table (nomogram, space-model, n-d-M method No correction was to be applied to $\%C_A$ and M.

ART 2

log ν_{20} = 2.000			log ν_{20} = 2.500			Nomogram			Space-model		n-d-M method		M_{exp}	Corr* for S
%C_A	%C_N	M	%C_A	%C_N	M	%C_A	%C_N	M	%C_A	%C_N	%C_A	%C_N		
						11	34	149	11	38	11	34	159	
						12	34	154	11	35	12	36	155	
						12	34	161	13	35	12	35	165	
						13	35	169	13	34	13	35	171	
						14	34	175	15	32	15	34	176	
						16	34	183	15	33	15	35	187	
						17	33	192	17	32	17	34	193	
						18	33	201	16	31	19	34	200	
						19	31	211	19	29	20	30	209	
						19.5	31	223	19	28	20	29	222	
						20	28	238	20	27	20	27	243	
						21	28	265	21	27	21	27	266	
23	22	353				24	26	298	24	25	24	24	306	—1
						14	24.5	159	15	25	15	21	165	
						15	24	167	15	23	16	20	173	
						17	22	177	18	21	18	19	181	
						19	22	185	19	20	20	18	188	
						19.5	21	193	20	18	21	18	194	
						20	20	203	21	19	20	18	209	
						19	19	216	20	18	20	18	213	
						17	18	231	17	17	17	16	237	
						15	17	244	14	16	15	14	260	
						13	15	265	13	16	13	15	280	
						12	15	333	11	14	12	17	340	
11	12	456				12	15	378	12	17	12	18	375	
						12	41	178	12	41	12	47	175	—1
						17	39	212	17	41	18	39	205	—3
						20	36	454	20	37	21	35	248	—4
22	37	307				22	32	304	22	31	22	31	304	—5
25	42	280	23	34	349	22	26	374	23	27	24	28	353	—6
						7	27	165	8	27	9	26	162	
						9	26	179	9	27	10	26	174	—1
						10	25	193	11	24	12	26	186	—1
						13	25	209	13	24	14	25	201	—1
						13	25	227	14	26	15	26	220	—2
						15	23	243	15	23	16	23	242	—3
						17	22	275	17	21	17	21	273	—4
						17	20	302	17	20	18	21	300	—4
25	27	324	23	22	412	23	16	429	23	18	22	16	434	—5
						9	30	166	10	32	11	30	164	
						11	29	178	12	30	12	29	176	
						13	27	192	13	26	15	28	187	
						15	26	212	16	25	17	27	201	
						16	24	231	16	25	17	27	220	—1
						15	23	255	15	22	16	25	246	—1
						16	22	294	16	21	16	24	276	—1
5	16	421				16	21	329	16	22	17	23	304	—1
7	21	393				17	22	372	17	23	17	22	345	—1
9	25	370	17.5	19	472	18	21	426	18	21	18	22	401	—1

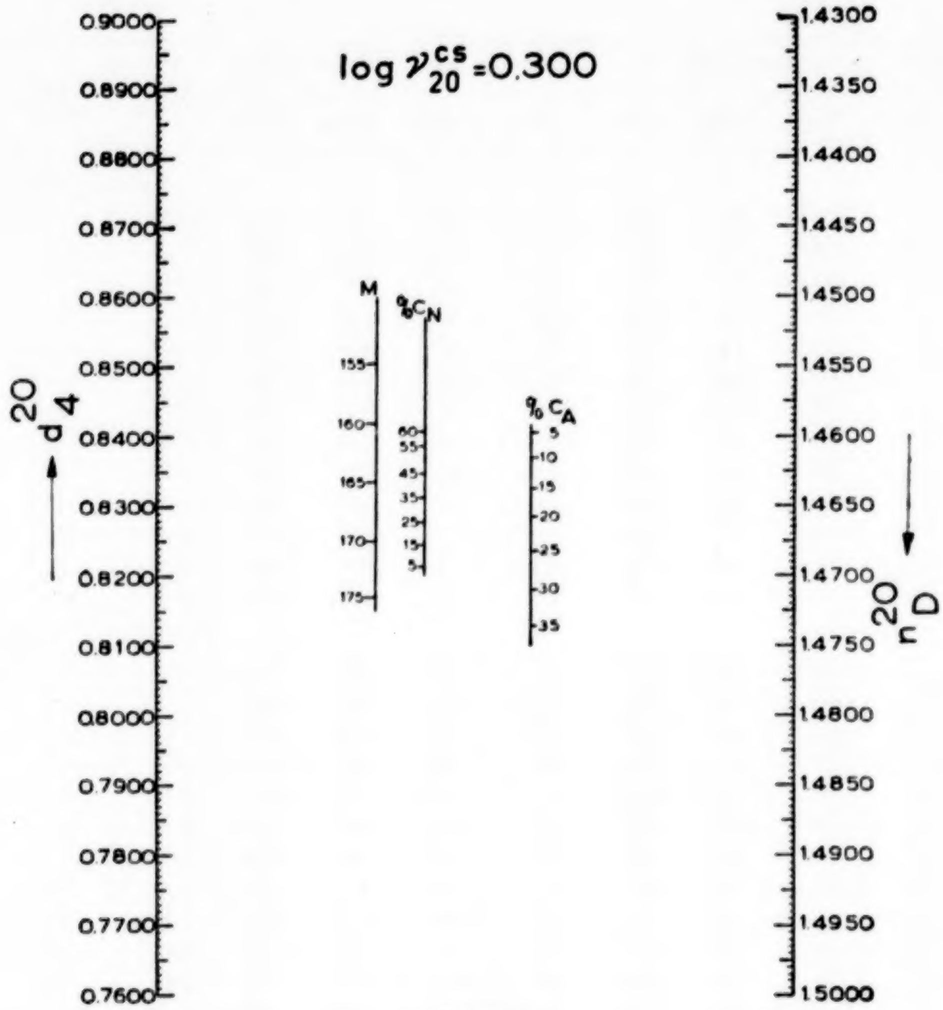

Fig. 1. Nomogram of the cross-section of the log ν-n-d space model for log ν_{20}^{cs} = 0.300.

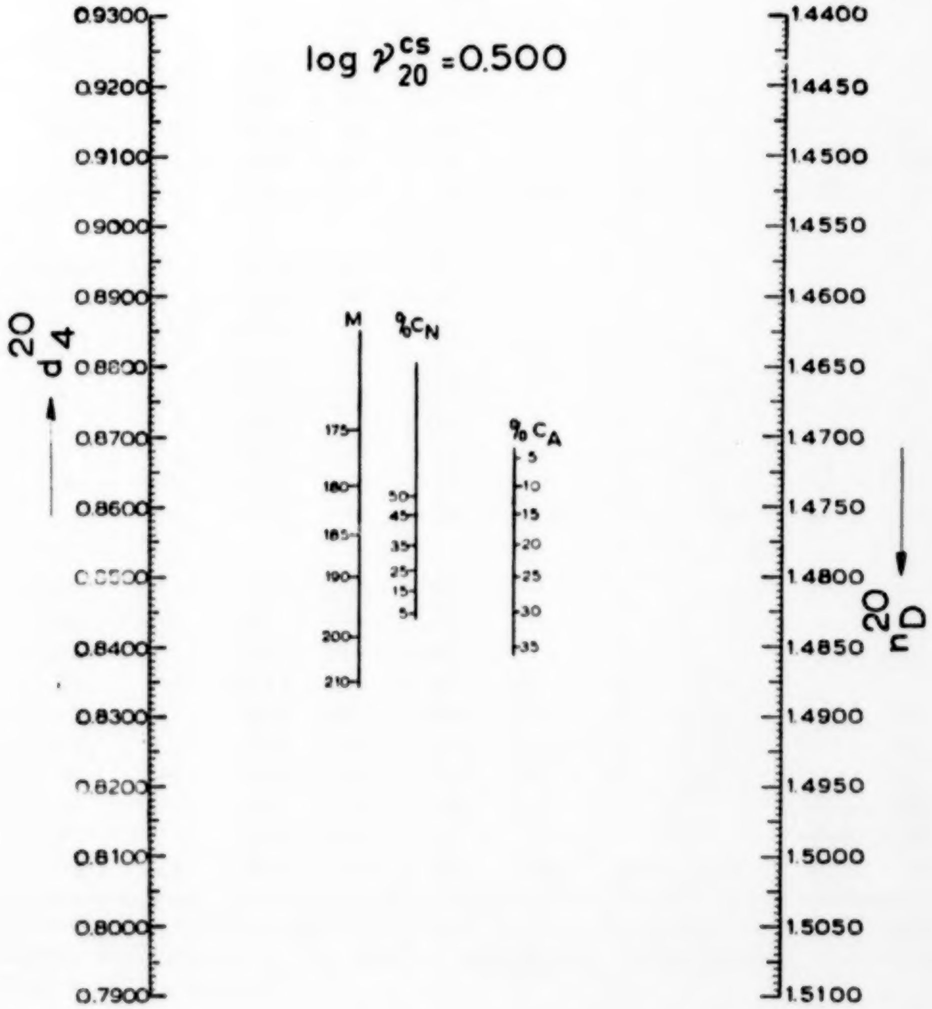

Fig. 2. Nomogram of the cross-section of the log ν-n-d space model for log ν_{20}^{cs} = 0.500.

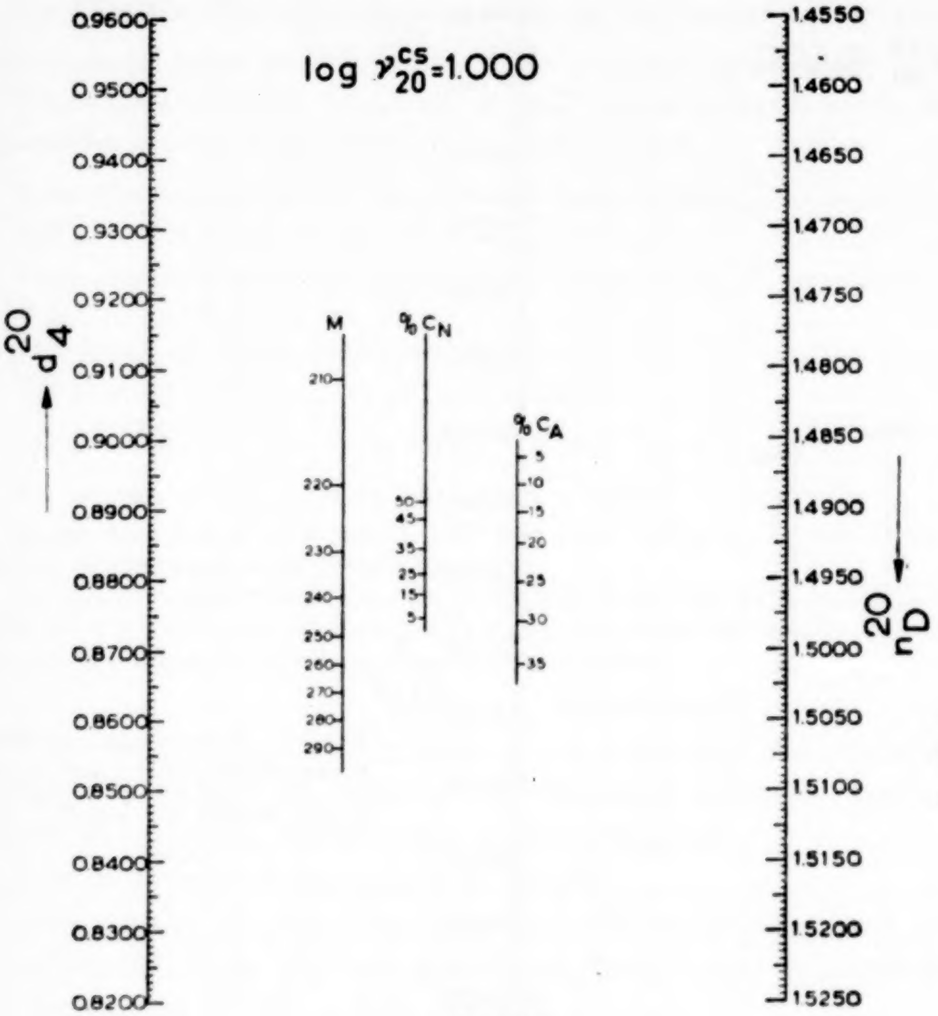
log ν_{20}^{cs}=1.000
d_4^{20}
0.9600
0.9500
0.9400
0.9300
0.9200
0.9100
0.9000
0.8900
0.8800
0.8700
0.8600
0.8500
0.8400
0.8300
0.8200
M
210
220
230
240
250
260
270
280
290
% C_N
50
45
35
25
15
5
% C_A
5
10
15
20
25
30
35
1.4550
1.4600
1.4650
1.4700
1.4750
1.4800
1.4850
1.4900
1.4950
1.5000
1.5050
1.5100
1.5150
1.5200
1.5250
n_D^{20}

Fig. 3. Nomogram of the cross-section of the log ν-n-d space model for log ν_{20}^{cs} = 1.000.

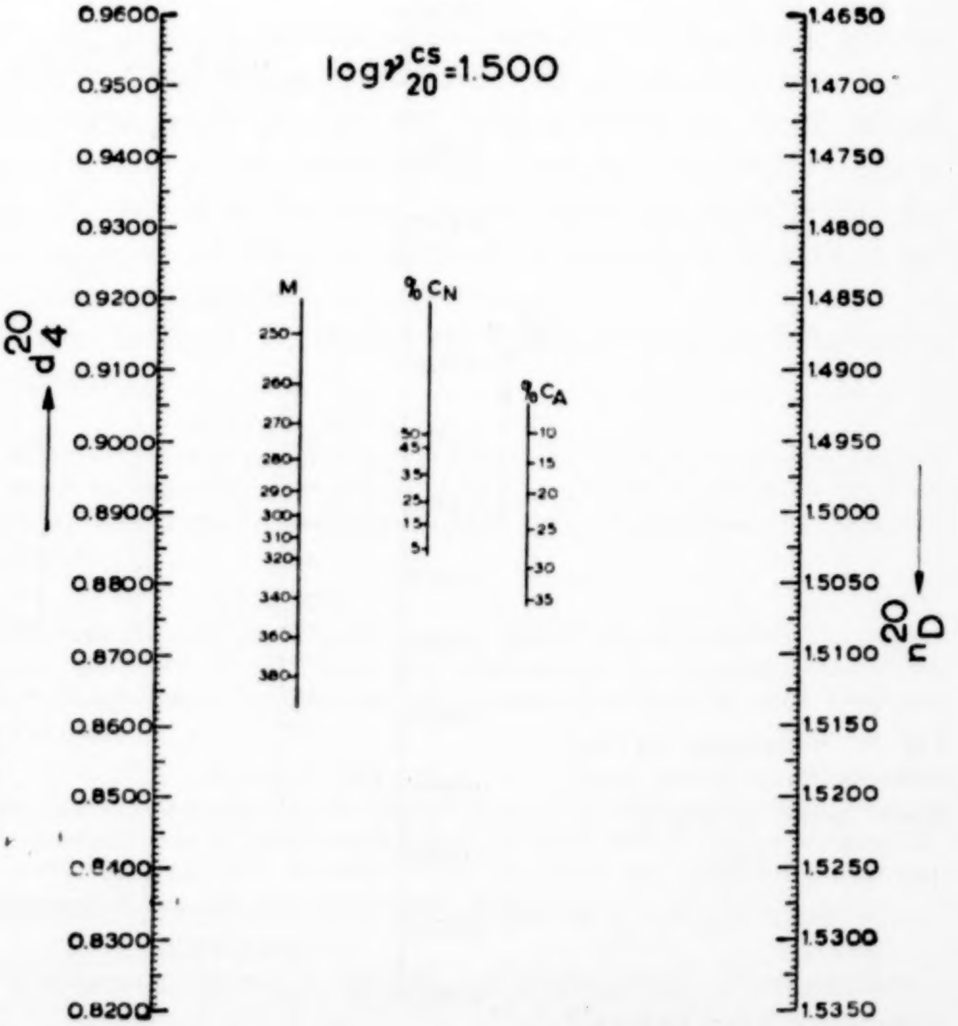
log ν_{20}^{cs}=1.500
d_4^{20}
0.9600
0.9500
0.9400
0.9300
0.9200
0.9100
0.9000
0.8900
0.8800
0.8700
0.8600
0.8500
0.8400
0.8300
0.8200
M
250
260
270
280
290
300
310
320
340
360
380
% C_N
50
45
35
25
15
5
% C_A
10
15
20
25
30
35
1.4650
1.4700
1.4750
1.4800
1.4850
1.4900
1.4950
1.5000
1.5050
1.5100
1.5150
1.5200
1.5250
1.5300
1.5350
n_D^{20}

Fig. 4. Nomogram of the cross-section of the log ν-n-d space model for log ν_{20}^{cs} = 1.500.

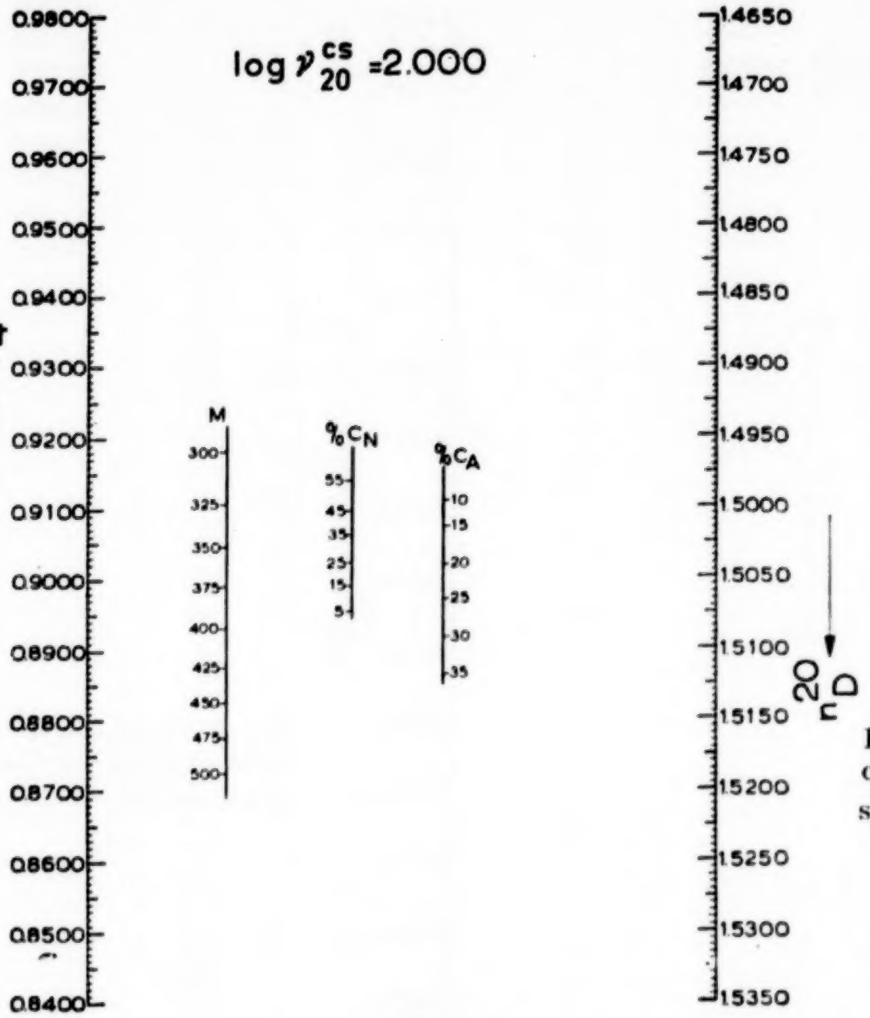
$\log \nu_{20}^{cs} = 2.000$
d_4^{20}
0.9800
0.9700
0.9600
0.9500
0.9400
0.9300
0.9200
0.9100
0.9000
0.8900
0.8800
0.8700
0.8600
0.8500
0.8400
M
300
325
350
375
400
425
450
475
500
%C_N
55
45
35
25
15
5
%C_A
10
15
20
25
30
35
n_D^{20}
1.4650
1.4700
1.4750
1.4800
1.4850
1.4900
1.4950
1.5000
1.5050
1.5100
1.5150
1.5200
1.5250
1.5300
1.5350

Fig. 5. Nomogram of the cross-section of the log ν-n-d space model for log ν_{20}^{cs} = 2.000.

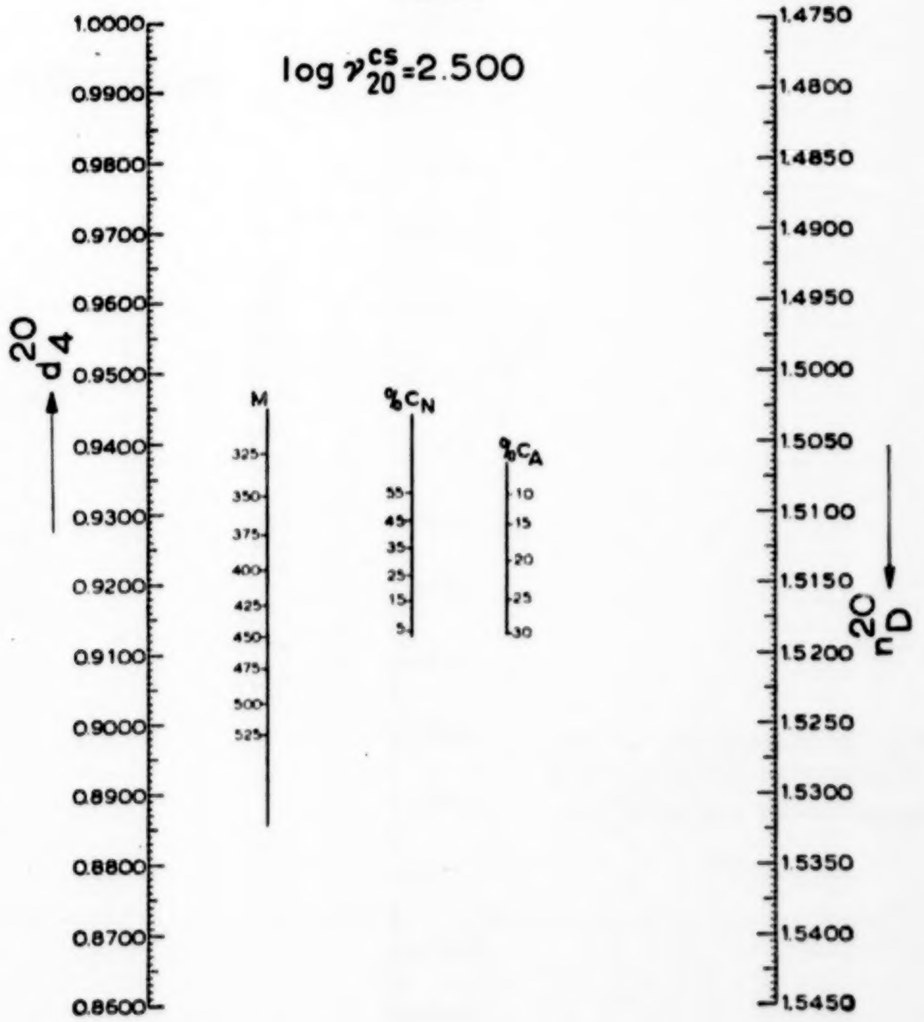
$\log \nu_{20}^{cs} = 2.500$
d_4^{20}
1.0000
0.9900
0.9800
0.9700
0.9600
0.9500
0.9400
0.9300
0.9200
0.9100
0.9000
0.8900
0.8800
0.8700
0.8600
M
325
350
375
400
425
450
475
500
525
%C_N
55
45
35
25
15
5
%C_A
10
15
20
25
30
n_D^{20}
1.4750
1.4800
1.4850
1.4900
1.4950
1.5000
1.5050
1.5100
1.5150
1.5200
1.5250
1.5300
1.5350
1.5400
1.5450

Fig. 6. Nomogram of the cross-section of the log ν-n-d space model for log ν_{20}^{cs} = 2.500.

As the value of $\log \nu_{20}^{cs}$ is equal to 0.828 the two nearest nomograms which have to be used are those which have been constructed for constant values of $\log \nu_{20}^{cs} = 0.500$ and $\log \nu_{20}^{cs} = 1.000$.

The values of $\%C_A$, $\%C_N$ and M read (linear interpolation is permitted) from those nomograms by means of the values of n_D^{20} and d_4^{20} are:

from the nomogram for the constant value of $\log \nu_{20}^{cs} = 0.500$:

$\%C_A = 17$; $\%C_N = 29$; $M = 191$;

from the nomogram for the constant value of $\log \nu_{20}^{cs} = 1.000$:

$\%C_A = 12$; $\%C_N = 18$; $M = 262$.

It follows by linear interpolation that

$$\%C_A = 17 - \frac{0.328}{0.500} \cdot 5 = 17 - 3 = 14,$$

$$\%C_N = 29 - \frac{0.328}{0.500} \cdot 11 = 29 - 7 = 22,$$

$$M = 191 + \frac{0.328}{0.500} \cdot 71 = 191 + 47 = 238.$$

From the n-d-M analysis it followed that $\%C_A = 15$ and $\%C_N = 22$. The experimental value of the molecular weight was 232.

It can be concluded from this result and from the data given in Table I that the determination of the carbon-type composition and the molecular weight can accurately be done by means of the nomograms given in this communication.

CONCLUSION

The use of the nomograms in determining the carbon-type composition and molecular weight of mineral oil fractions must be given priority to the use of the cross-sections which they replace because

1. the nomograms are easier to handle,
2. the results obtained by means of the nomograms are more accurate than those obtained from the cross-sections, both being compared to the data obtained by means of the n-d-M analysis.
3. the nomograms give a rapid characterization of the mineral oil fractions; several physical constants and structural elements can be read simultaneously.

It must nevertheless be borne in mind that the cross-sections are more or less indispensable for the construction of the nomograms. Besides the cross-sections give a better insight into the shape of the space model than the nomograms do. The space model remains the basis of the new method. However for practical application the nomograms are recommended.

The authors' thanks are due to Mr. J. F. HENGEVELD for his valuable help in the construction of the nomograms.

SUMMARY

Nomograms are presented from which it is possible to determine the carbon-type composition and molecular weight of mineral oil fractions by means of the measured viscosity, refractive index and density. The nomograms replace the cross-sections of the space model which has recently been introduced by the authors[1].

RÉSUMÉ

Des nomogrammes sont présentés au moyen desquels il est possible de déterminer la composition et le poids moléculaire de fractions d'huile minérale, connaissant la viscosité, l'indice de réfraction et la densité. Les nomogrammes remplacent les sections du modèle dans l'espace, proposé récemment par les auteurs.

ZUSAMMENFASSUNG

In dieser Arbeit werden Nomogramme gegeben, die es ermöglichen, die Kohlenwasserstoff-Zusammensetzung und das Molekulargewicht von Mineralölfraktionen zu bestimmen, deren Viskosität, Brechungsindex und Dichte bekannt sind. Die Nomogramme ersetzen die Schnitte durch ein kürzlich von den Verfassern eingeführtes dreidimensionales Modell.

REFERENCE

[1] J. CORNELISSEN AND H. I. WATERMAN, *Chimie & industrie*, to be published; *Brennstoffchem.*, to be published.

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DETERMINATION OF MERCURY VIA REDUCTION WITH HYDRAZINE

by

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This paper describes an improved procedure for the determination of mercury based on reduction to the elemental state by hydrazine in ammoniacal medium. The earlier studies of this reaction have been reviewed by WILLARD AND BOLDYREFF[3]. These and previous investigators concluded the determination by weighing the mercury, which is inconvenient and involves considerable loss by volatilization. In the present method the more convenient and accurate technique of dissolving the mercury in nitric acid and titrating with standard thiocyanate solution is employed.

By reducing the mercury from an ammoniacal solution containing tartrate ion as a sequesterant, the determination can be done in the presence of copper, bismuth, lead, cadmium, arsenic, antimony, and tin. Thus the procedure is applicable to the hydrogen sulfide group precipitate, and is well adapted to a systematic analytical scheme.

PROCEDURE

Standard solutions of mercuric nitrate were prepared from both pure mercuric oxide and metallic mercury. The potassium thiocyanate titrant solution (*ca.* $0.05M$) was standardized by using it to titrate the standard mercuric nitrate solution in the usual way[1].

A 0.5 to 1 g sample — which in a systematic analysis would be the hydrogen sulfide group precipitate and may contain up to about 200 mg of mercury — is dissolved in a 50 ml centrifuge tube in 8 ml of hot 1:1 ($6M$) hydrochloric acid. If necessary a small amount (0.5 ml) of nitric acid may be added to effect complete solution.

To this sample solution is then added, all at once, 20 ml of a solution of 2 g of sodium tartrate dihydrate in 1:1 ($7M$) ammonia. The solution is cooled to below about 35°, and 5 ml of $0.2M$ hydrazine sulfate ($N_2H_4 \cdot H_2SO_4$) solution is added, and the mixture is stirred. After standing until reduction and precipitation of the mercury is complete (30 min usually is adequate) the mixture is centrifuged, and the supernatant solution is drawn off through a sintered glass filter stick. The mercury is washed with water until chloride ion has been completely removed. Because chloride ion interferes with the thiocyanate titration of mercury its complete removal is essential.

The washed mercury is dissolved in 1 to 2 ml of concentrated nitric acid, and, after diluting to about 10 ml, the solution is boiled briefly to remove oxides of nitrogen, transferred to a 100 ml Erlenmeyer flask, and diluted to about 50 ml. After cooling to below 20°, 1 ml of $0.3M$ ferric alum (or ferric nitrate) is added, and the solution is titrated with standard thiocyanate solution[1].

PERFORMANCE DATA

Data obtained in the determination of mercury in the presence of large amounts of copper, bismuth, lead, cadmium, tin, arsenic, and antimony are shown in Table I. In general the error averages only a few tenths of a percent. The tendency toward a small systematic negative error indicates a slight loss of mercury by volatilization.

TABLE I

DETERMINATION OF MERCURY IN PRESENCE OF OTHER HYDROGEN SULFIDE GROUP ELEMENTS

Mercury		*Error*	*Other elements present*
taken *mg*	*found* *mg*	%	*mg*
144.0	143.9	−0.1	None
144.0	143.5	−0.3	150 Cd
144.0	144.5	+0.3	100 Cd
141.6	141.4	−0.2	200 Pb
139.7	140.0	+0.3	150 Pb
185.8	185.5	−0.2	150 Cu
182.5	181.5	−0.5	100 Cu
134.7	134.1	−0.5	200 Bi
144.3	143.3	−0.7	150 Bi
144.0	143.5	−0.3	220 Sn
144.0	144.7	+0.5	200 Sn
144.0	143.8	−0.2	200 As
144.0	143.6	−0.3	150 As
162.1	160.9	−0.7	100 Sb
188.9	187.2	−0.9	150 Sb

The reduction of mercury salts by hydrazine apparently is autocatalytic. There is usually an induction period of a few minutes after the hydrazine is added before visible precipitation of mercury begins. This induction period can be greatly shortened by warming the solution, but this is inadvisable because it is likely to lead to serious loss of mercury by volatilization. The induction period at room temperature is short enough not to be troublesome, and once the reaction begins it proceeds rapidly to completion. A total time of 30 minutes was found to be ample for complete reduction in all cases. Complete reduction is indicated by cessation of turbidity and a clearing of the supernatant solution.

With the constant concentration (*ca.* 1.2*M*) of ammonium ion produced in the foregoing procedure the concentration of excess free ammonia may vary from 1 to 3*M* with no effect on either the rate of precipitation of mercury or the accuracy of the results.

Assuming that the hydrazine is oxidized to nitrogen, according to $N_2H_4 + 4\ NH_3 = N_2 + 4\ NH_4^+ + 4\,e$, each 1 ml of 0.2*M* hydrazine sulfate solution is sufficient to reduce 80 mg of +2 mercury. In agreement with this we found that a large excess of hydrazine is not necessary and the quantity specified in the procedure (5 ml of 0.2*M*) is ample with up to 200 mg of mercury.

In the presence of copper reduction of mercury begins immediately with little or no induction period. This catalytic effect doubtless stems from the fact that the cupric tartrate complex is reduced quite rapidly by hydrazine to the cuprous state (diammino cuprous ion) and the cuprous copper reduces +2 mercury more rapidly than does hydrazine. With a very large quantity of copper (*e.g.*, 500 mg) and a large excess of hydrazine, metallic copper eventually precipitates. However, with the amount of hydrazine specified (5 ml of 0.2*M* per 40 ml) reduction does not proceed below the cuprous state.

When the ammoniacal tartrate solution is added to a hydrochloric acid solution of the sample white, flocculent $Hg(NH_3)_2Cl_2$ precipitates. This causes no difficulty, since it is readily reduced to metallic mercury when the hydrazine is added. In the absence of halide ions the mercury remains in solution, presumably as the diammino mercuric cation. In ammoniacal tartrate-chloride medium +3 antimony reduces the +2 mercury to mercurous chloride and mercury. This in itself is not deleterious since complete reduction to elemental mercury results after the hydrazine is added. However, the +5 antimony formed partially precipitates, presumably as Sb_2O_5. In this event the mixture of mercury and antimonic oxide is centrifuged, washed, and the mercury is dissolved in nitric acid as usual. The mercuric nitrate solution is then separated from the residue of antimonic oxide by centrifugation or filtration, and titrated. If an antimony determination is desired the residual antimonic oxide is transferred to the original filtrate from the mercury reduction, and on acidification and treatment with hydrogen sulfide it will be metathesized to antimony trisulfide.

This procedure is readily adaptable to a systematic analysis of the hydrogen sulfide group. The solution remaining from the removal of mercury can be acidified with hydrochloric acid to a free hydrogen ion concentration of about 0.3*M*, and the remaining elements precipitated with hydrogen sulfide. The precipitate may then be analysed by any of the customary procedures, such as that of Swift[2].

It should also be possible to separate copper, bismuth, lead, and cadmium from arsenic, antimony and tin by directly treating the ammoniacal filtrate from the mercury precipitation with hydrogen sulfide. The filtrate from the precipitation of the copper group sulfides can then be acidified to precipitate the sulfides of arsenic, antimony, and tin.

Of the other elements of the hydrogen sulfide group, silver, gold, selenium, tellurium, and the platinum metals are more or less reduced to the elemental state under the conditions of the mercury determination, and are potential interferences. However, when hydrochloric acid is used to decompose the sample the silver chloride can be removed from the diluted acid solution before precipitation of the mercury. Since gold and the platinum metals are insoluble in the nitric acid used to dissolve the mercury they should not interfere. Selenium and tellurium probably will be oxidized by the nitric acid to soluble selenous acid and slightly soluble tellurous acid, and the influence (if any) of these on the titration of mercury has not been established.

SUMMARY

A convenient, accurate method for the determination of mercury is described, based on reduction to the elemental state by hydrazine in an ammoniacal solution containing tartrate ion. The precipitated mercury is dissolved in nitric acid and titrated with standard thiocyanate solution. The method is applicable in the presence of copper, bismuth, lead, cadmium, arsenic, antimony, and tin, and most other elements of the hydrogen sulfide group.

RÉSUMÉ

Une méthode précise est décrite pour le dosage du mercure; elle est basée sur sa réduction à l'état élémentaire, par l'hydrazine, en solution ammoniacale renfermant des ions tartriques. Le mercure précipité est dissous dans l'acide nitrique et titré par une solution étalon de thiocyanate. Cette méthode peut être utilisée en présence de cuivre, de bismuth, de plomb, de cadmium. d'arsenic, d'antimoine, d'étain et de la plupart des autres éléments du groupe de l'hydrogène sulfuré.

ZUSAMMENFASSUNG

Eine genaue Quecksilberbestimmungsmethode wird beschrieben; sie gründet sich auf die Reduktion der Quecksilberionen zu elementarem Quecksilber mit Hilfe von Hydrazin in ammoniokalischer Lösung und in Gegenwart von Tartrationen. Das gefällte Quecksilber wird in Salpetersäure gelöst und mit einer Thiocyanat-Titerlösung titriert. Die Methode kann in Gegenwart von Kupfer, Wismuth, Blei, Cadmium, Arsen, Antimon, Zinn und der meisten anderen Elemente der Schwefelwasserstoffgruppe angewendet werden.

REFERENCES

[1] I. M. Kolthoff and J. J. Lingane, *J. Am. Chem. Soc.*, 57 (1935) 2126.
[2] E. H. Swift, *A System of Chemical Analysis*, E. H. Freeman Co., San Francisco, 1956.
[3] H. H. Willard and A. W. Boldyreff, *J. Am. Chem. Soc.*, 52 (1930) 569.

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THIOCYANATE INTERFERENCE IN THE PERMANGANOMETRY OF HYDROGEN PEROXIDE

by

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During the course of a reinvestigation on the kinetics of the H_2O_2-KSCN reaction[1], the classical permanganometric estimation of hydrogen peroxide was found to be impracticable owing to the reducing action of the thiocyanate ion. Since few direct titrimetric procedures are otherwise available, it was considered necessary to modify the above method for a rapid and accurate routine work. Preliminary experiments revealed that the interference due to SCN^- may be eliminated by adding deliberately to the system an excess of silver nitrate and precipitating the sparingly soluble silver thiocyanate. Based on this, a permanganometric determination of hydrogen peroxide in the presence of thiocyanate is described here.

EXPERIMENTAL

The hydrogen peroxide solution of desired concentration was obtained by appropriate dilution of the E. Merck's 20-volume sample and was standardized by titration with a $KMnO_4$ solution of known strength.

To a system containing an approximately known quantity of KSCN solution, a slight excess of silver nitrate solution, 20-25 ml of 2*N* sulphuric acid and an aliquot volume of hydrogen peroxide were added. A standard solution of permanganate was now run in until the appearance of the usual pink colour. Data of a representative set of experiments are entered in Table I. It will be seen that the results recorded by the present method are in agreement with those obtained by the standard method.

---

[1] J. H. Kastle and C. R. Smith, *Am. Chem. J.*, 32 (1904) 376.

TABLE I

Expt. No.	*Vol. of 0.1N KSCN taken ml*	*Vol. of 0.1N $AgNO_3$ added ml*	*Vol. of H_2O_2 ml*	*Vol. of 0.07651N $KMnO_4$ required ml*
1	—	—	5.0	13·75
2	—	—	10.0	27.50
3	5	10	5.0	13·75
4	10	15	10.0	27.50
5	20	30	10.0	27.50
(6	—	5	5.0	13·75)
(7	—	10	10.0	27·50)
(8	—	20	10.0	27·50)

Prior blank experiments were also performed with a view to examine the dependability of the $KMnO_4$ method of estimating hydrogen peroxide in the presence of silver nitrate. Results in parentheses (Table I) show that sufficiently large quantities of $AgNO_3$ have little adverse effect on the stoichiometry of the H_2O_2-$KMnO_4$ reaction. Further, it is interesting to note that the heavy precipitate of silver thiocyanate provides an excellent white background for a correct perception of the end-point. The data obtained by the application of the above method to the kinetic study of the H_2O_2-KSCN reaction will be communicated at a later stage.

The author is grateful to Professor S. S. Joshi for research facilities.

SUMMARY

The estimation of hydrogen peroxide in the presence of thiocyanate, based on the prior precipitation of the latter as the sparingly soluble silver salt and subsequent titration of H_2O_2 with standard permanganate, is described. The white precipitate of silver thiocyanate provides an excellent background for the perception of a correct end-point.

RÉSUMÉ

Un dosage du peroxyde d'hydrogène en présence de thiocyanate est décrit; il est basé sur la précipitation préalable du thiocyanate comme sel d'argent peu soluble; on titre ensuite H_2O_2 par une solution étalon de permanganate. Le précipité blanc de thiocyanate d'argent constitue un excellent fond pour percevoir un point final précis.

ZUSAMMENFASSUNG

Eine Methode zur Bestimmung von Wasserstoffperoxyd in Gegenwart von Thiocyanat wird beschrieben. Man fällt das Thiocyanat als schwerlösliches Silbersalz und titriert dann das H_2O_2 mit einer Permanganat-Titerlösung. Der weisse Silberthiocyanatniederschlag bildet einen ausgezeichneten Hintergrund zur deutlichen Erkennung des Endpunkts.

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THORIUM COMPLEX OF 2,7-DINITROSO-1,8-DIHYDROXYNAPHTHALENE-3,6-DISULPHONIC ACID

I. DETECTION AND VOLUMETRIC DETERMINATION OF THORIUM

by

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Thorium does not form coloured ions nor shows light absorption in the range 2000 te 10000 Å[1] so that few methods exist for the colorimetric determination for thorium[2]. The most important colorimetric reagent for thorium is thorin — 2-(2-hydroxy-3,6-disulpho-1-naphtylazo)-benzenearsonic acid — described by KUZNETSOV[3]. The reagent has been used successfully in the micro determination of thorium[4-9]. The alkannet used by FORMANEK[10] gives a violet colour with solutions of thorium and rare earth salts. A spectrophotometric method for the determination of thorium has been developed using naphthazarin (5,8-di-hydroxy-1,4-naphthoquinone)[1]. The nature and composition of this purple complex of thorium have been studied. MILTON *et al.*[11] have used the lake-forming chromazurol-S as an indicator in the titration of fluoride with thorium. It is also used[12,13] for the titration of thorium with EDTA. Alizarin red-S, carminic acid and ammonium purpurate have been recommended as colorimetric reagents for thorium[14]. WILLARD AND HORTON[15] describe the advantages and disadvantages of a number of dyes which react with thorium in the titration of fluoride. BANERJEE[16] has recently prepared 2-(*p*-sulphophenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid (SPADNS), which forms a blue-violet lake with thorium in acid solution. Similar dyes from chromotropic acid and diazotised naphthionic acid, namely 2-(4-sulphonaphthylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid (SNADNS), 2,7-bis-(4-sulphonaphthylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid (di-SNADNS) and nitroso-SNADNS, have been prepared by the author[17] and have been utilized in the determination of thorium by various methods.

The thorium complex of 2,7-dinitrosochromotropic acid or its tautomer, chromotropic acid dioxime is now discussed and the use of the reagent in the detection and volumetric determination of thorium with oxalic acid is described. This reagent has been used as a specific and highly sensitive reagent for cobalt[18], as little as 0.05 μg of cobalt giving a blue or blue-violet spot. It is also highly specific for nickel and copper. No mention is made in the literature regarding its use in the determination of thorium. The red aqueous solution of the substance turns to pinkish-violet in the presence of thorium in acid medium. In a concentrated solution of thorium a turbidity is formed with an excess of the reagent which on boiling becomes a violet

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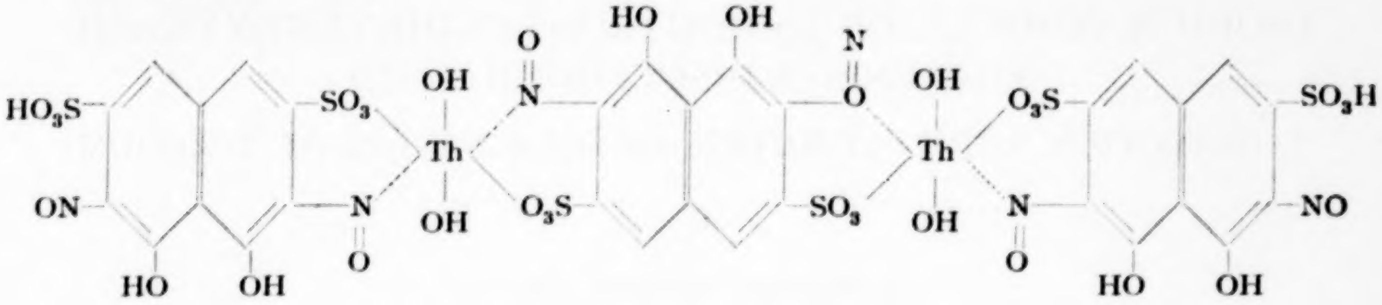
precipitate. This precipitation, however, is not quantitative. Analysis shows that the complex contains 2 thorium atoms for 3 reagent molecules. The composition of the complex may be as follows:



EXPERIMENTAL

Reagents and chemicals

Dinitrosochromotropic acid. Chromotropic acid (Na-salt) (36.4 g; 1 mole) and conc. HCl (80 ml) are placed in a litre flask, immersed in ice. The mixture is vigorously stirred, while a solution of sodium nitrate (17 g; 0.2 moles) in water (100 ml) is added slowly during 20-30 minutes. The temperature is maintained at or below 10° throughout the addition. A red-brown solution results. The mixture is stirred further for one hour and the solution is filtered. Absolute alcohol is then added to the filtrate with stirring, until the precipitation is complete. The deep chocolate precipitate is filtered off, washed with alcohol and dried. The dinitrosochromotropic acid is purified by repeated dissolution in the minimum amount of water and reprecipitation with absolute alcohol.

Thorium nitrate. A stock solution is prepared from Merck's thorium nitrate tetrahydrate and is standardized gravimetrically with 2:4-D[19].

Stock solutions of other metals are prepared from their soluble A.R. salts and standardized by conventional methods.

Buffer solutions are made by mixing different amounts of *N* sodium acetate and *N* HCl.

Precipitation of thorium complex

A thorium solution containing 0.0216 g or more of thorium dioxide was brought to the boil and an excess of a 1% aqueous solution of the reagent was added. The mixture is boiled for 10 minutes and then allowed to stand for half-an-hour. The violet precipitate which settled at the bottom of the beaker was filtered off, washed several times with 0.05% reagent solution and then with a small quantity of ice-cold water. The precipitate was dried at 110° and then ignited in a platinum crucible to a constant weight of thorium dioxide. The process was repeated with thorium solutions of different pH values adjusted with buffer solutions, in order to find out the most suitable pH values for maximum thorium recovery. The results are given in Tables I and and II.

TABLE I

PRECIPITATION LIMIT AND RECOVERY OF THORIUM FROM SOLUTION

Total volume = 30 ml

ThO_2 taken g	*Reagent (1%)* ml	*ThO_2 found* g	*Recovery* %
0.0216	2	0.0010	4.2
0.0216	4	0.0032	14.8
0.0216	5	0.0048	22.2
0.0216	8	0.0098	45.4
0.0216	10	0.0100	46.3
0.0270	12	0.0126	46.8
0.0324	15	0.0149	46.1
0.0108	6	0.0023	21.3
0.0094	6	0.0003	3.2
0.0081	6	nil	—

TABLE II

EFFECT OF PH ON THE PRECIPITATION OF THORIUM

ThO_2 taken = 0.0216 g, reagent (1%) = 10 ml

pH	*ThO_2 found* g	*Recovery* %	*pH*	*ThO_2 found* g	*Recovery* %
1.2	0.0008	3.7	3.3	0.0092	42.5
1.8	0.0018	8.4	3.5	0.0100	46.3
2.1	0.0032	14.8	3.8	0.0109	50.4
2.4	0.0051	23.6	4.1	0.0112	51.8
2.8	0.0082	38.0	4.3	0.0111	51.4
4.6	0.0102	47.2	5.0	0.0084	38.9

The above tables show that the salt is not precipitated from a solution containing less than 9.4 mg of ThO_2 per 30 ml; the maximum quantity of thorium in the form of ThO_2 that can be recovered in the solid state is only 51.8 % at pH 4.1.

Properties of thorium complex

The thorium complex of dinitrosochromotropic acid is deep violet in colour in the solid state, but in aqueous solution the colour is pinkish-violet. It is soluble in ethyl and methyl alcohols and in acetone, but is insoluble in other organic solvents. It is soluble in acids, alkalis and in solutions of ammonium acetate and ammonium carbonate.

Composition of the thorium complex

A quantity of the thorium salt was precipitated from a concentrated solution of thorium and was washed several times with ice-cold water in which the salt is less soluble. It was dried at 110°C to a constant weight. Aliquot amounts of the salt were ignited to thoria. Nitrogen was determined in a portion of the salt by the standard method. From the data it appear that 2 atoms of thorium are associated with three molecules of the reagent. (Found : ThO_2 = 32.08%, N_2 = 4.86%; $(C_{30}H_{18}O_{34}N_6S_6)Th_2$ requires ThO_2 = 31.8% and N_2 = 5.05%).

Spot test analysis for thorium

Dinitrosochromotropic acid produces a pinkish-violet coloration with thorium in dilute solution. In order to test the sensitivity of this reagent for the identification of thorium by visual methods, spot tests were done in micro test tubes or spot plates or by filter paper methods[20].

Procedure

A drop of the test solution of thorium at pH 4 was placed in a micro test tube and to it was added a drop of 0.05% aqueous solution of the reagent. A blank was prepared at the same time with a drop of water in place of the test solution to compare the colour. A definite colour change showed a positive result with the sample. Similar tests were performed on the spot plate. The results showed that 1 μg of thorium could be identified in this way.

Spot test on filter paper

A drop of the reagent (0.05%) was placed with the help of a micro pipette on a piece of a chromatographic filter paper: the paper was partially dried in air and then a drop of the test solution was placed at the centre of the spot and again partially dried in air. The results are noted below:

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TABLE III

FILTER PAPER SPOT TEST FOR THORIUM

Spot: reagent alone	*Spot: reagent + test solution*	*Limiting sensitivity*
Pale red spot with a narrow buff-coloured ring at the rim.	Red spot becoming pink at the centre and surrounded by a white broad ring with a narrow buff-coloured ring at the rim.	2.5

Volumetric determination of thorium with oxalic acid

Oxalic acid is a standard reagent for thorium and forms a white insoluble precipitate of thorium oxalate. GOOCH AND KABAYASHI[21] determined thorium by precipitating it as oxalate and then titrating the latter with potassium permanganate solution. Another method consists in adding the thorium solution to a known excess of oxalate and then titrating the remaining oxalate with a standard thorium nitrate[22]. The direct volumetric procedure for the estimation of thorium with oxalic acid in presence of alizarin-S as an indicator, was developed by VENKATESWARLU AND RAMNATHAN[23] and it was successfully applied by the author[17] in determining thorium using the dyes: SNADNS, di-SNADNS and nitroso-SNADNS. The same method was applied with the present reagent as an indicator. The principle of the method is that thorium forms a pinkish-violet coloured complex with dinitrosochromotropic acid which is not very stable and can be destroyed by the addition of standard oxalic acid. The colour change at the end-point is from pinkish-violet to red, indicating that all the thorium has been converted to thorium oxalate The method is useful for very dilute solutions of thorium from which no appreciable precipitation of thorium oxalate takes place.

Procedure

An aliquot part of thorium solution was taken in an erlenmeyer flask and the acidity was adjusted by adding 0.1*N* HCl; 2 ml of the reagent solution (0.05%) were then added to it and the mixture was diluted to 50 ml and heated to 60°C to complete the reaction. It was then rapidly titrated with standard oxalic acid solution using a microburette for the titration. At the end-point the colour of the solution changed sharply from pinkish-violet to red. The results are recorded in Table IV. As the amount of oxalate precipitate increases, the end-point becomes obscure and a considerable amount of absorption takes place.

TABLE IV

TITRATION OF THORIUM WITH OXALIC ACID

Thorium nitrate = 0.0152*M*, oxalic acid = 0.0201*M*

Thorium taken mg	*Oxalic acid added ml*	*Oxalic acid reqd. ml*	*Difference ml*
3.53	1.68	1.57	+0.11
1.77	0.87	0.79	+0.08
5.29	2.95	2.36	+0.59
2.65	1.27	1.18	+0.09
1.32	0.66	0.59	+0.07
4.85	2.31	2.16	+0.15
7.06	3.96	3.14	+0.82
7.50	4.25	3.34	+0.91
8.82	4.73	3.73	+1.00
10.59	5.92	4.72	+1.20

Effect of hydrogen ion concentration

Oxalic acid reacts with thorium in mineral acid solution, but the thorium complex is unsuitable at high acid concentrations; it was thus necessary to find a suitable pH range convenient to both. Titrations were carried out in solutions, the pH of which was carefully adjusted by adding buffer solutions and measuring by means of pH-meter. The results in Table V indicate that the pH range 3-3.8 is suitable for the titration.

TABLE V

TITRATION OF THORIUM AT DIFFERENT PH

Thorium taken = 4.85 mg

pH	*Oxalic acid added (0.0201 M) ml*	*Thorium found mg*	*Difference mg*
1.6	0.06	0.14	—4.71
2.0	1.21	2.82	—2.03
2.2	1.50	3.38	—1.47
2.5	1.82	4.09	—0.76
3.1	2.01	4.52	—0.33
3.3	2.07	4.66	—0.19
3.6	2.11	4.75	—0.10
3.8	2.18	4.91	+0.06
4.0	2.08	4.68	—0.17

Study of interferences

Interferences in the titration of thorium with oxalic acid in presence of the reagent are: mercury(I), tin(II), lead, copper, iron(III) and zirconium. Other metals when present in smaller quantities do not appear to interfere in the titration. Some representative results are shown in Table VI.

TABLE VI

EFFECT OF DIVERSE IONS IN THE TITRATION

Thorium taken = 3.53 mg, oxalic acid = 0.0201 *M*, pH = 3

Metal	*Quantity mg*	*Th found mg*	*Metal*	*Quantity mg*	*Th found mg*
Cd^{+2}	4.3	3.23	Zn^{+2}	3.1	3.28
Hg^{+2}	2.9	3.42	Mn^{+2}	3.4	3.47
Ba^{+2}	5.1	3.30	Ni^{+2}	4.7	3.33
Ca^{+2}	3.9	3.38	Co^{+2}	5.0	3.38
Al^{+3}	5.3	3.46	Au^{+3}	2.1	3.32
Mg^{+2}	2.7	3.31	Ti^{+4}	4.3	3.45
Sr^{+2}	4.3	3.38	U^{+6}	2.2	3.27

ACKNOWLEDGEMENT

The author takes this opportunity of expressing his indebtedness to Dr. N. B. BOSE, Principal of the College, Dr. S. K. SINHA, Head of the Department of Chemistry and to Mr. G. BANERJEE, his colleague, for their helpful suggestions and interest in the work.

SUMMARY

Dinitrosochromotropic acid has been used as a new reagent for the determination of thorium. It forms a pinkish-violet thorium complex which is highly soluble in water and in which two

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atoms of thorium are associated with three molecules of the reagent. The complex may be precipitated from a concentrated solution of thorium with an excess of the reagent and the maximum quantity of the thorium complex that may be recovered in the solid state is only 51.8% at pH. 4.1 The smallest amounts of thorium that may be detected with this reagent by spot test on the spot plate and on filter paper are respectively 1.0 μg and 2.5 μg. Thorium has also been successfully determined volumetrically using oxalic acid in the presence of this reagent in the pH range 3-3.9; common metals like cadmium, barium, calcium, aluminium *etc.* do not interfere.

RÉSUMÉ

L'acide dinitrosochromotropique a été proposé comme nouveau réactif pour la détermination du thorium. Il forme avec le thorium un complexe rose-violet très soluble dans l'eau et contenant deux atomes de thorium pour trois molécules de réactif. Le complexe peut être précipité d'une solution concentrée de thorium par un excès de réactif, la quantité maximum de complexe pouvant être récupérée à l'état solide étant 51.8% à un pH de 4.1. Les quantités minima qu'il est possible de déceler par ce réactif à la touche sur plaque de porcelaine ou sur papier filtre sont respectivement 1.0 μg et 2.5 μg. Le thorium a également été déterminé avec succès par la méthode volumétrique en employant l'acide oxalique en présence de ce nouveau réactif dans le domaine de pH de 3 à 3.9; les métaux ordinaires tels que le cadmium, le barium, le calcium, l'aluminium etc. ne gènent pas.

ZUSAMMENFASSUNG

Die Dinitrosochromotropsäure wurde als ein neues Reagenz für die Bestimmung von Thorium vorgeschlagen. Sie bildet mit Thorium eine stark wasserlösliche rosa-violette Komplexverbindung welche 2 Atome Thorium für ja 3 Moleküle Reagenz enthält. Diese kann aus einer konzentrierten Thoriumlösung mit einem Überschuss an Reagenz gefällt werden, die maximale Menge welche im festen Zustand gewonnen werden kann beträgt aber nur 51.8% bei pH 4.1. Die kleinsten Thoriummengen, welche mit diesem Reagenz nachgewiesen werden können, sind 1 μg auf der Tüpfelplatte und 2.5 μg auf Filtrierpapier. Das Thorium konnte auch volumetrisch mit Oxalsäure in Gegenwart des neuen Reagenzes im pH-Bereich 3 bis 3.9 erfolgreich bestimmt werden; die gewöhnlichen Metalle wie Cadmium, Barium, Calcium, Aluminium usw. stören nicht.

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THORIUM COMPLEX OF 2,7-DINITROSO-1,8-DIHYDROXYNAPHTHALENE-3,6-DISULPHONIC ACID

II. SPECTROPHOTOMETRIC DETERMINATION OF THORIUM

by

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In part I of this series dinitrosochromotropic acid has been found to produce a pinkish-violet complex with thorium[1] which is highly soluble in water. From the gravimetric analysis it appears that a 2:3 thorium-reagent complex is formed in the reaction. The present paper describes the spectrophotometric determination of thorium with this reagent. The spectral curve of the thorium complex exhibits an absorption maximum at 370 mμ. The colour system conforms to Beer's law and is very stable for a long period.

EXPERIMENTAL

Reagents and chemicals

Reagent solution. A 0.05% solution of the reagent in water was used in the determination.

Thorium nitrate. A stock solution of thorium nitrate tetrahydrate (Merck) was prepared and was standardized with 2:4-D[2]. The standard solutions used in this work were made by appropriate dilution of aliquots of this stock solution.

Buffer solution. Buffer mixtures of various pH were prepared by mixing requisite amounts of *N* HCl with *N* sodium acetate.

Stock solutions of certain metals were prepared by dissolving definite quantities of soluble A.R. salts of the metals in water, the metal contents of the solutions being determined by standard methods.

Apparatus. Absorbance measurements were made with a Beckman spectrophotometer, model DU, using 1 cm cells. A Muirhead-type pH meter was used for pH measurements.

Colour reaction and spectral curves

The reaction of thorium with dinitrosochromotropic acid was found to give a pinkish-violet colour which develops very rapidly and remains stable for a considerable period. The complex was formed by transferring about 100 μg of thorium to a 25 ml volumetric flask and adding successively 0.5 ml of 1 *N* HCl and 1 ml of the reagent (0.05%) and then the volume was made up to the mark with distilled water. A blank was similarly prepared, water being added in place of thorium solution. Absorbance measurements of the thorium complex were carried out at various wavelengths in the spectrophotometer against distilled water and then against the blank solution. The absorbance of the reagent was also measured against a water blank. The spectral curves as shown in Fig. 1, reveal that the complex has an absorption peak at 370 mμ, when measured against a reagent blank solution. The absorbance of the reagent at this wave length is slight.

Optimum conditions for the determination of thorium

Effect of pH

In order to determine a suitable acid concentration for the determination, a series of solutions containing a definite quantity of thorium and the reagent were adjusted to various pH values from 0.8 to 5.0 with HCl and buffer mixtures. The absorbance of each of these solutions was measured against a reagent blank at 370 mμ; the values indicated by curve A in Fig. 2, show that the absorbance increases with the increase of pH up to 3.0 and then decreases gradually with further rise in the pH. Curve B shows the effect of pH on the absorbance of an aqueous

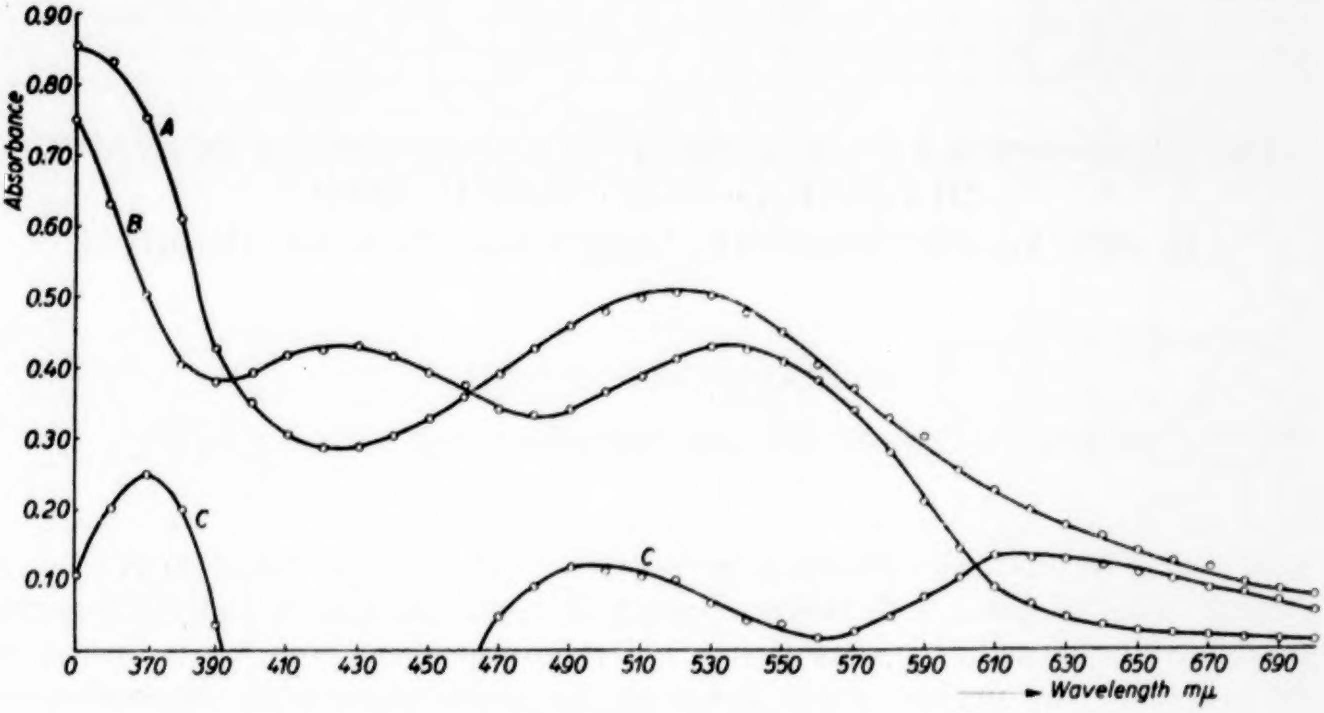

Fig. 1. Spectral curves for Th-complex and the reagent. A = Th-complex *vs* water; B = Reagent *vs* water; C = Th-complex *vs* reagent.

solution of the reagent measured against a distilled water blank. From the nature of the curves it appears that a pH range from 2.5 to 3.4 is suitable for the determination of thorium, as the absorbance of the thorium complex is nearly constant and maximum in this range, while that of the reagent is small.

Concentration of the reagent

Different quantities of the reagent solution (0.05%) were added to a definite amount of thorium and diluted to volume. Absorbance values of these solutions were measured at 370 mμ against a reference solution of the reagent. It was observed that at pH 2.5, 1.5 ml of 0.05% reagent solution was sufficient to complex 77 μg of thorium per 10 ml solution. Further increase in the concentration of the reagent produces a slight change in the absorbance values, a large excess of the reagent, however, masks the colour of the complex.

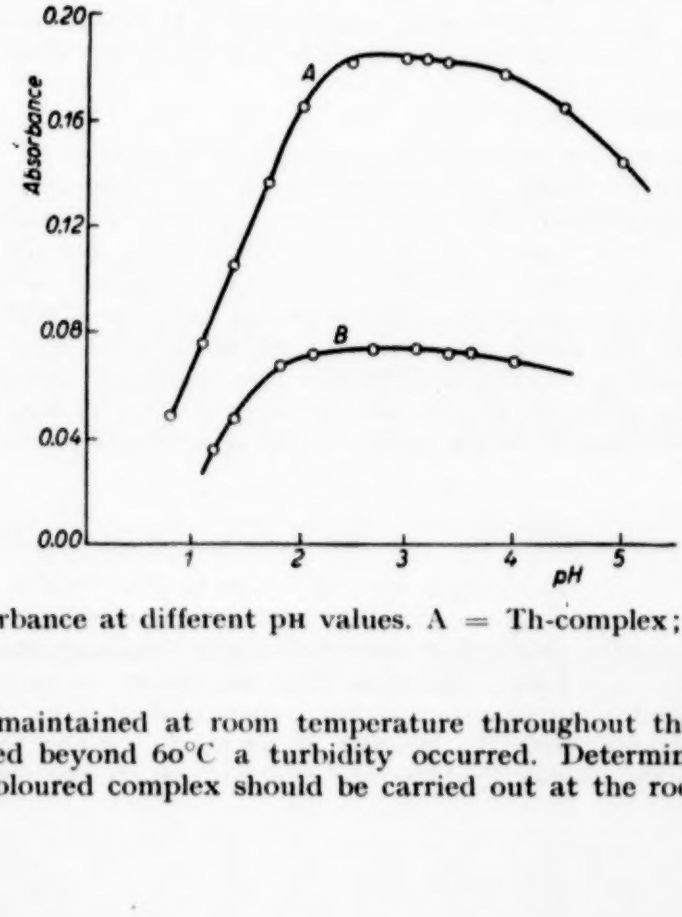

Fig. 2. Absorbance at different pH values. A = Th-complex; B = Reagent.

Effect of temperature

The solutions were maintained at room temperature throughout the experiment. When a test solution was heated beyond 60°C a turbidity occurred. Determination of thorium after the formation of the coloured complex should be carried out at the room temperature.

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Stability of the colour system

To test stability of the colour in the aqueous medium, the colour of a solution containing 51 μg of thorium per 10 ml, was developed and the absorbance measured at different intervals of time. It was observed that the thorium complex was stable for more than a day, after which a slight turbidity appeared. In more concentrated solutions of thorium, however, a turbidity developed in a shorter period.

Preparation of the calibration curve

In order to determine whether the coloured thorium complex obeys Beer's law, a calibration curve was prepared by measuring the optical density at 370 mμ of solutions containing different amounts of thorium and reagent at pH 2.5. The standard curve obtained (in the absence of interfering ions) is a straight line passing through the centre. Thus, conformity of the coloured solutions to Beer's law is excellent for amounts of thorium in the range 0.03-200 μg per 10 ml of solution. With higher concentrations of thorium, a turbidity or precipitation occurs (see Fig. 3).

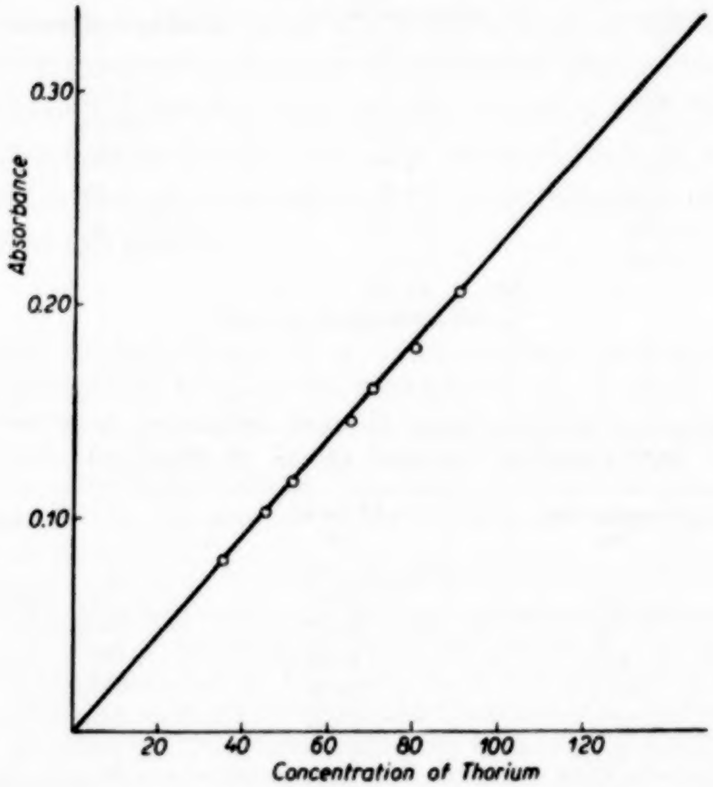

Fig. 3. Calibration curve at pH 2.5.

Sensitivity of the reaction

The sensitivity of the colour reaction in the determination of thorium was determined by measuring the absorbance of solutions of reagent containing gradually decreasing amounts of thorium. The practical limit of sensitivity of the reaction was found to be 0.03 μg per ml.

Analytical procedure for the determination of thorium

Aliquot parts of a standard solution of thorium were transferred to 25 ml volumetric flasks to which a quantity of 0.05% solution of the reagent (1.5 ml per 0.77 mg of Th) was added. The solution was diluted to nearly 25 ml, the pH was adjusted to 2.5 by adding 0.1*N* HCl and then water was added to make the volume 25 ml. The blank was prepared by diluting the same amount of the reagent (0.05%) with water to 25 ml, the pH being adjusted to 2.5. The absorbance was measured in a 1-cm cuvette in the spectrophotometer against the reagent blank at a wavelength 370 mμ. In a range of concentrations from 35 to 90 μg of thorium in a volume of 10 ml, as shown in Table I, the mean percentage of deviation in the absorbance index is 1.61%, the absorbance index being determined as:

$$A_s = \frac{A}{C \cdot b},$$

where, A_s = absorbance index
A = measured absorbance
b = length of the absorbing layer of material in cm
C = concentration in grams per litre solution.

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Effect of diverse ions

The effects of other ions were examined in the determinations of thorium. The metals added to the thorium solutions were: copper, cadmium, lead, mercury, iron, chromium, aluminium, calcium, barium, zirconium, titanium, uranium and gold. The anions added were: chloride, nitrate, sulphate, fluoride, phosphate, cyanide and citrate. Absorbance measurements of these mixtures containing requisite amounts of the reagent revealed that very little interference was caused by the presence of the metals cadmium, mercury(II), aluminium, zinc, titanium, cerium (III), gold, uranium and the anions nitrate, chloride and sulphate. The alkaline earth metals showed some bleaching effect. Copper, nickel, cobalt, chromium caused slight interference. Heavy interference was caused by iron, zirconium, cerium(IV) phosphate, fluoride, cyanide and citrate. The results are given in Table II. All the measurements were carried out at pH 2.5.

TABLE I

ABSORBANCE INDEX OF THORIUM-DINITROSOCHROMOTROPIC ACID COMPLEX

Th µg	*Absorbance* *A*	*Absorbance index* A_s	*Deviation from average*	%
35	0.081	23.14	—0.02	0.09
45	0.104	23.11	—0.05	0.22
65	0.141	24.00	+0.84	3.63
70	0.160	22.80	—0.36	1.55
80	0.183	22.80	—0.36	1.55
90	0.208	23.10	—0.06	0.26
		Av. 23.16		

% of deviation = 1.61

TABLE II

EFFECT OF CERTAIN FOREIGN IONS ON THE DETERMINATION OF THORIUM

(All solutions contain 51 µg of thorium)

Ions	*Amount present* mg	*Th found* µg	*Remarks*
Cd^{+2}	3.0	51.0	No interference
Cu^{+2}	2.3	51.2	Slight ,,
Hg^{+2}	4.1	50.9	No ,,
Fe^{+3}	2.5	52.7	Heavy ,,
Cr^{+3}	4.3	51.2	Slight ,,
Al^{+3}	3.1	51.0	No ,,
Ca^{+2}	5.1	48.9	Bleaching
Ba^{+2}	3.4	49.0	,,
Mg^{+2}	2.8	49.9	,,
Zn^{+2}	3.3	51.1	No interference
Ce^{+3}	2.5	51.0	,, ,,
Ce^{+4}	3.1	52.5	Heavy ,,
Co^{+2}	3.4	51.2	Slight ,,
Ni^{+2}	4.4	51.2	,, ,,
Ti^{+4}	5.1	50.8	No ,,
Zr^{+4}	4.3	52.9	Heavy ,,
U^{+6}	3.5	50.7	No ,,
Au^{+3}	2.4	51.2	Slight ,,
NO_3^-	5.4	51.1	No ,,
SO_4^{-2}	4.6	50.8	,, ,,
Cl^-	4.1	51.0	,, ,,
Br^-	3.9	50.7	,, ,,
PO_4^{-3}	2.9	51.6	Slight ,,
CN^-	2.4	51.5	,, ,,
F^-	3.9	21.0	Heavy ,,
citrate	2.3	33 1	,, ,,

DISCUSSION

Microgram quantities of thorium form a pinkish-violet complex with dinitrosochromotropic acid in mineral acid medium. The colour system obeys Beer's law

References p. 425.

when absorbance measurements are made at 370 mμ. At this wavelength the absorbance value of the complex is maximum while that of the reagent is small. The coloured product is fairly stable but on long standing it becomes turbid and a gradual increase in the absorbance occurs. Thorium may be suitably determined at pH 2.5-3.4 with this reagent; the complex is unstable in high acid concentration. A large excess of the reagent should not be added during measurements as this masks the colour of the thorium complex. The colour reaction is extremely sensitive; as little as 0.03 μg/ml of thorium may be determined by this method. The reagent is specific for thorium under the given conditions except that some coloured ions like copper, cobalt, nickel, *etc.*, absorbing at this wavelength, present some minor difficulties. Zirconium, iron, cerium(IV) interfere seriously in the determination, while the alkaline earth metals cause some bleaching of the colour. Anions which react with thorium (phosphate, fluoride and citrate) also cause serious interference in the method. These interfering ions should be removed, if present, before the determination of thorium is carried out. The method may be suitably applied with slight modification for the spectrophotometric determination of thorium in minerals like monazite and black sands.

ACKNOWLEDGEMENT

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SUMMARY

Dinitrosochromotropic acid has been used for the spectrophotometric determination of thorium. The thorium complex of the reagent shows an absorbance maximum at 370 mμ. The colour system conforms to Beer's law and is stable for a considerable period. The determination of thorium by this method is accurate and rapid and the reagent is sensitive to 0.03 μg of thorium per ml. The pH range suitable for the determination is from 2.5 to 3.4. A number of ions do not interfere but zirconium and iron are among the ions which exhibit strong interference and should be removed before applying this method.

RÉSUMÉ

L'acide dinitrosochromotropique a été utilisé pour le dosage spectrophotométrique du thorium. Le complexe obtenu présente une absorption maximum à 370 mμ. La coloration obéit à la loi de Beer, elle est stable relativement longtemps. Le dosage du thorium par cette méthode est précis et rapide. Le reactif est sensible: L'on peut déceler jusqu'à 0.03 γ de Th par ml. Le pH doit être compris entre 2.5 et 3.4. De nombreux ions ne gênent pas, mais d'autres, dont le zirconium et le fer, perturbent la réaction et doivent être éliminés au préalable.

ZUSAMMENFASSUNG

Die Dinitrosochromotropsäure wurde zur spektrophotometrischen Thoriumbestimmung verwendet. Die Komplexverbindung zwischen diesem Reagenz und Thorium zeigt ein Absorptionsmaximum bei 370 mμ. Die Absorption folgt dem Beer'schen Gesetze. Die Farbe ist längere Zeit stabil. Die Methode ist genau und rasch; es können bis zu 0.03 μg Th pro ml erfasst werden. Der günstigste pH -Bereich ist 2.5 bis 3.4. Eine Anzahl Ionen stören nicht aber andere, worunter Zirkonium und Eisen, stören stark und müssen daher vor Ausführung der Bestimmung abgetrennt werden.

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DETERMINATION OF LEAD SULFATE BY MEANS OF CATION EXCHANGERS

by

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INTRODUCTION

A simple and accurate method for determining the amount of sulfuric acid in lead sulfate, is described by TREADWELL[1]. The analysis is performed in the following manner: Lead sulfate is boiled with a solution of sodium carbonate and after cooling, the solution is saturated with carbon dioxide and the precipitate is filtered off. By this treatment the lead present is completely precipitated as lead carbonate according to the reaction formula:

$$PbSO_4 + Na_2CO_3 \rightarrow PbCO_3 + Na_2SO_4$$

In the filtrate the sulfate is precipitated and weighed as barium sulfate.

In this paper a way of simplifying this analytical method is described in which the timeconsuming precipitation and weighing of barium sulfate is avoided, a procedure which moreover often leads to errors because of the risk of occlusion when the analysis is not performed with the utmost care[2]. The method of analysis is the same as described above until the lead carbonate has been filtered off. The filtrate is then passed through a cation exchanger of sulfonic acid type in the hydrogen form, when the following reaction occurs ($R\text{-}SO_3H$ means the cation exchanger in the hydrogen form):

$$Na_2SO_4 + 2\ R\text{-}SO_3H \rightarrow 2\ R\text{-}SO_3Na + H_2SO_4$$

In the solution that has passed through the ion exchange column the amount of sulfate can be determined by titration of the liberated sulfuric acid with standard sodium hydroxide solution.

EXPERIMENTAL

The ion exchange columns used were of ordinary type[3], with a height of 140 mm and a diameter of 10 mm of the resin bed. The cation exchanger used was the strongly acid Amberlite IR-120 (Rohm and Haas Company) with a particle size of 0.15-0.30 mm in air dry condition. The resin was converted to the hydrogen form by treatment with 150 ml of 3-4*N* hydrochloric acid.

The experiments were performed in the following manner: Varying accurately weighed amounts of lead sulfate (analytical reagent grade, dried at 150°C) were boiled for one hour in a solution of 0.50 g of sodium carbonate in about 200 ml distilled water. After cooling, the solution was saturated with carbon dioxide and the lead carbonate formed was filtered off, and was washed with water saturated with carbon dioxide. The combined filtrate and wash water thus contained sodium sulfate and sodium carbonate, because an excess of sodium carbonate must be used for the precipitation of the lead carbonate. It was therefore not appropriate to percolate the solution directly through the ion exchange column because carbon dioxide evolved when the sodium carbonate reacted with the hydrogen saturated resin caused channeling in the resin bed and might prevent the passage of the solution[4]. Therefore the filtrate was first boiled with the resin in a beaker for about twenty minutes. After cooling, the solution and the resin were poured into the ion exchange column, containing a short layer, about 2-3 cm in height, of the hydrogen saturated cation exchanger, which removed the last traces of cations. Afterwards the resin was washed with 50 ml distilled water. The combined effluent and wash water was boiled for twenty minutes in order to drive off the last traces of carbon dioxide and after cooling the solution was titrated with 0.1 *N* sodium hydroxide solution with phenolphthalein as indicator. When a solution, containing only sodium carbonate, was treated as described above, no consumption of sodium hydroxide occurred, *i.e.* all the carbon dioxide was driven off.

The results which are given in Table I show that the accuracy of the method is very high, a maximum error of ± 0.4% being obtained.

TABLE I

$PbSO_4$ added	*$PbSO_4$ found*	*Relative error %*
0.2012	0.2017	+ 0.25
0.3123	0.3118	— 0.16
0.4002	0.3995	— 0.18
0.4510	0.4491	— 0.42
0.4998	0.5002	+ 0.08

APPLICATIONS

The method outlined above has been used for the determination of lead sulfate in plates of lead-acid batteries. As is known the lead-acid battery consists of a positive plate of lead peroxide and a negative plate of lead in an electrolyte of sulfuric acid. The reactions occurring in this battery are in accordance with the present generally accepted double-sulfate theory:

$$PbO_2 + Pb + 2\,H_2SO_4 \rightleftarrows 2\,PbSO_4 + 2\,H_2O$$

This equation represents the discharge from left to right and the charge in the opposite direction.

As seen from the reaction formula lead sulfate is normally formed on both plates at the discharge of the battery. This sulfate is finely crystalline and easily reduced when charging the battery. The concept of sulfation, however, applies to the lead sulfate formed on the plates when the battery is not handled in a proper manner[5]. Sulfation in this meaning may depend on different causes, among others that the battery is allowed to stand in a discharged condition for a long time or that the battery is operated at excessive temperatures.

Because the sulfation is very injurious to the battery it is important to determine the degree of sulfation. The determination was performed in the following way: The plates were washed free from sulfuric acid and were dried. Pieces of the plates, weighing about 6 g were accurately weighed and boiled for one hour in about 200 ml water containing 0.5 g sodium carbonate; this is equivalent to 1.4 g lead sulfate, *i.e.* about 25% of the weight of the sample. As the battery plate usually contains about 5-10% lead sulfate this amount of sodium carbonate is sufficient. After cooling, the solution was saturated with carbon dioxide and the precipitated lead carbonate filtered off, and the analysis was performed as described above. The results are given in Table II, along with the values which are obtained when the sulfate is precipitated as barium sulfate.

TABLE II

Sample No.	% $PbSO_4$	
	determined as $BaSO_4$	*determined by the ion exchange method*
1	1.22	1.23 1.24
2	4.92	4.96
3	2.75	2.73

As seen from Table II good agreement is obtained between the two methods which appear to have a similar accuracy. However, the ion exchange method has the advantage of requiring only a simple titration and may therefore be preferred, at least in laboratories where ion exchange methods are generally used.

SUMMARY

A method for the determination of lead sulfate is described using the following procedure: The lead sulfate is boiled in a solution of sodium carbonate; after cooling, the solution is saturated with carbon dioxide and the precipitated lead carbonate is filtered off. The filtrate is boiled with a strongly acid cation exchanger in the hydrogen form and after cooling, the solution and resin are poured into an ion exchange column, containing a short layer of resin. After washing with water the combined filtrate and wash water is titrated with $0.1N$ sodium hydroxide using phenolphthalein as indicator.

The method is accurate and gives a maximum relative error of ± 0.4%. The procedure described above has been used for determination of the degree of sulfation in lead-acid battery plates.

RÉSUMÉ

Une méthode est décrite pour le dosage du sulfate de plomb. Ce dernier est chauffé à ébullition dans une solution de carbonate de sodium. Après refroidissement, la solution est saturée d'anhydride carbonique et le précipité de carbonate de plomb formé est filtré. Le filtrat obtenu est porté à ébullition avec un échangeur de cation fortement acide; après refroidissement la solution et la résine sont versées sur une colonne d'échange d'ions renfermant une petite couche de résine. Après rinçage à l'eau, le filtrat (+ eau de lavage) est titré au moyen d'une solution d'hydroxyde de sodium $0.1N$, en présence de phénolphtaléine comme indicateur.

La méthode est précise et donne une erreur relative maximum de ± 0.4%. Elle permet de déterminer le degré de sulfatation des plaques de batteries plomb-acide.

ZUSAMMENFASSUNG

Eine Bestimmungsmethode für Bleisulfat wird beschrieben. Das Bleisulfat wird in Natriumcarbonatlösung gekocht; nach dem Erkalten wird die Lösung mit Kohlendioxyd gestättigt und das gefällte Bleicarbonat abfiltriert. Das Filtrat wird mit einem stark sauren Ionenaustauscher in der Wasserstofform gekocht; nach dem Erkalten werden Lösung und Harz in eine Ionenaustauschersäule gegossen, die eine kleine Lage Harz enthält. Nach dem Waschen mit Wasser werden die kombinierten Filtrate und Waschwässer mit $0.1N$ NaOH in Gegenwart von Phenolphthalein als Indikator titriert.

Die Methode ist genau; der maximale relative Fehler beträgt ± 0.4%. Das Verfahren wurde zur Bestimmung des Sulfatationsgrades von Blei-Säure-Batterie-Platten angewendet.

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REQUIRED COOLING PERIOD FOR PORCELAIN CRUCIBLES IN DESICCATORS

by

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INTRODUCTION

It is well known that the apparent weight of warm objects deviates from the correct mass on the low side. Consequently special care is required in the weighing of crucibles which have been previously heated. The specifications given in various textbooks to ensure the absence of errors from this cause vary widely. In the case of porcelain crucibles the recommended cooling period in the desiccator varies from 25-45 minutes; sometimes it is advised to cool the crucibles in air for one or two minutes before placing them in the desiccator. It was observed that often these specifications caused serious errors, especially when quick weighings were made. Therefore an experimental investigation was required to elucidate this point and this, together with some theoretical investigations is presented here.

THEORETICAL CONSIDERATIONS

As a first approximation the establishment of equilibrium of a cooling object with its surroundings can be represented by the following simple mathematical derivations.

For not too large differences in temperature it may be assumed that the heat transport and consequently the rate of change of temperature is proportional to the temperature difference with the surroundings. Consequently the heat loss, and also the decrease in temperature in an increment of time d*t* is represented by

$$\mathrm{d}T = -k'\,(T_0 - T_r)\,\mathrm{d}t \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

k' is a proportionality factor, determining the speed of heat transmission

T_0 is the initial temperature of the hot object

T_r is the room temperature

Choosing the room temperature as a point of reference gives:

$$\mathrm{d}T = -k'T\mathrm{d}t \quad \ldots\ldots\ldots\ldots\ldots \quad (1a)$$

T is the temperature difference between object and room. Integrating gives:

$$T = T_0.\mathrm{e}^{-k't} \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

T_0 is the initial temperature difference and t the time elapsed after the beginning to reach temperature T.

For calculations it is easier to use the logarithmic formula

$$\ln T = \ln T_0 - k't \quad \text{. . . . . (3)}$$

or, if $k = 0.43\ k'$

$$\log T = \log T_0 - kt \quad \text{. . . . . (3a)}$$

Theoretically, temperature equilibrium is established asymptotically; in practice the problem is to find a compromise between the extremes of too short a cooling period and undue loss of time.

EXPERIMENTAL

Experiments were carried out:

1. On the cooling-rate of crucibles in desiccators to verify the above theoretical considerations. From these experiments will be found the time necessary under varying conditions to reach a certain temperature difference between crucibles and room.
2. On the effect of temperature difference on the apparent weight of the crucibles.

1. Experiments on cooling

Two types of crucibles were used: A with a mean weight of *ca.* 18 g, and B with a mean weight of *ca.* 13 g, both of 45 mm diameter. Two or seven crucibles were placed in a desiccator, either after the glowing red heat had only just disappeared (from 5-10 seconds after removal of the flame) or after a cooling period of one minute in free air. The moment of placing the last crucible in the desiccator was taken as the beginning of the cooling period. A desiccator was used with diameter and height both about 17 cm, wall thickness 10 mm, cover thickness 4 mm, distance between porcelain plate and bottom *ca.* 6 cm. The lower compartment was partly filled with sulfuric acid. The temperature inside the desiccator was measured with a thermometer fixed in a rubber stopper through the central opening of the cover. The mercury reservoir of the thermometer was placed near the bottom of a crucible placed in the centre of the desiccator. The desiccator was placed immediately in a room kept at constant temperature.

Obviously the temperature readings do not coincide with the actual temperature of the crucibles which, moreover, are not uniform throughout, but it is assumed that they represent the situation adequately.

Results

A number of experimentally obtained values are represented in Figures 1, 2 and 3. Because the number of values in an experiment was more than two, and there are

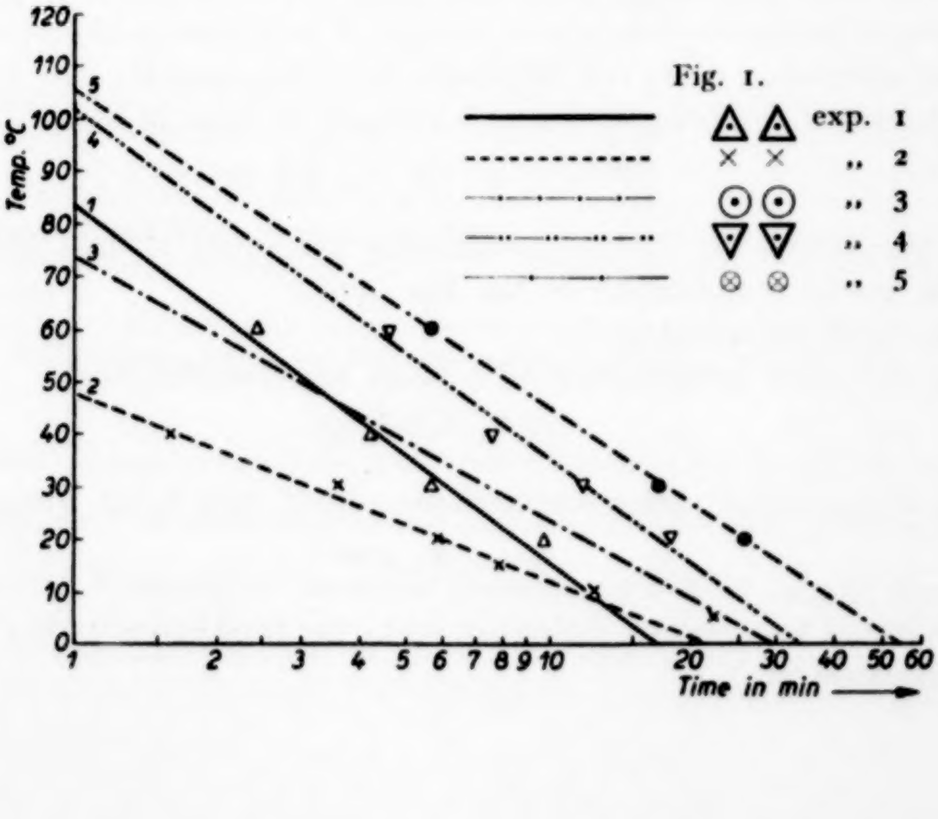

Fig. 1.

only two constants k and T_0 in the formula, the most probable values for these constants were calculated with the method of least squares.

The next part of the investigation concerned the cooling period required to obtain a certain difference between inner and outer temperature. Differences of 5°C, 2°C and 1°C were chosen and denoted by t_5, t_2 and t_1. The values calculated from k and T_0 are represented in Table I and summarized in Table II.

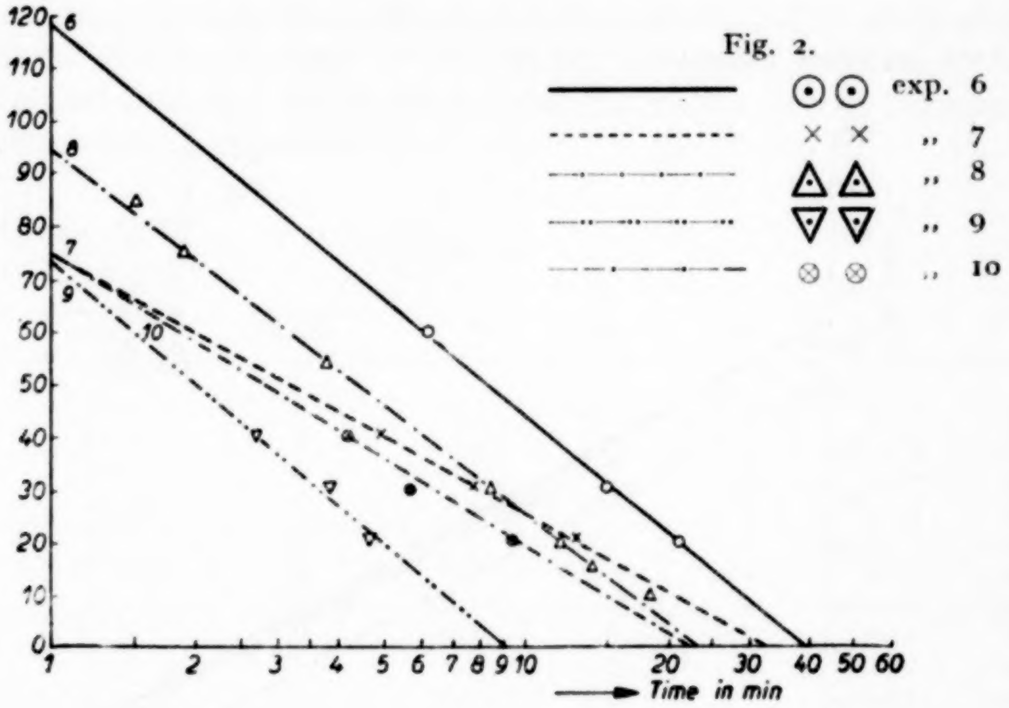

Fig. 2.

TABLE I

Number of experiment	number	Crucibles type	pretreatm.*	T_0**	k	t_1	t_2	t_5	Remarks
1	2	A	M	17	0.015	84	64	36	
2	2	B	M	22	0.028	48	37	23	***
3	7	B	M	30	0.020	74	59	39	
4	7	A	M	34	0.015	102	82	57	
5	7	A	R	55	0.017	105	87	62	
6	7	B	R	39	0.013	119	96	66	
7	7	A	M	32	0.021	75	60	40	
8	7	A	M	23	0.014	96	76	54	
9	2	B	M	9	0.013	73	50	20	
10	2	B	R	22	0.018	76	60	36	
11	2	A	R	28	0.020	74	59	38	
12	7	B	R	47	0.020	85	69	49	****
13	7	B	R	42	0.019	84	70	47	****
14	7	A	R	47	0.021	79	65	51	****

* M indicates that the crucibles have been cooled on the porcelain triangle for one minute, before being placed in the desiccator, R indicates that they have been placed in it immediately after cooling below redness.

** It should be noted that the value of T_0 given here is not the actual temperature read at the beginning of the experiment, but a mean temperature of the system of crucibles and desiccator. It takes about ten minutes before the readings of the thermometer agree with the straight lines of Figures 1, 2 and 3.

*** Not used for further calculations. See text.

**** Air sucked through the desiccator during cooling. See text.

TABLE II

Number of experiment	*Crucibles Number*	*Crucibles Pretreatm.**	T_0	*mean* T_0	t_1	*mean* t_1
5,6	7	R	55,39	47	105,119	112
3,4,7,8,	7	M	30,34,32,23	30	74,102,75,96	87
10,11	2	R	22,28	25	76,74	75
1,9	2	M	17,9	13	84,73	79
12,13,14****	7	R	47,42,47	45	85,84,79	83

* and **** see notes Table I.

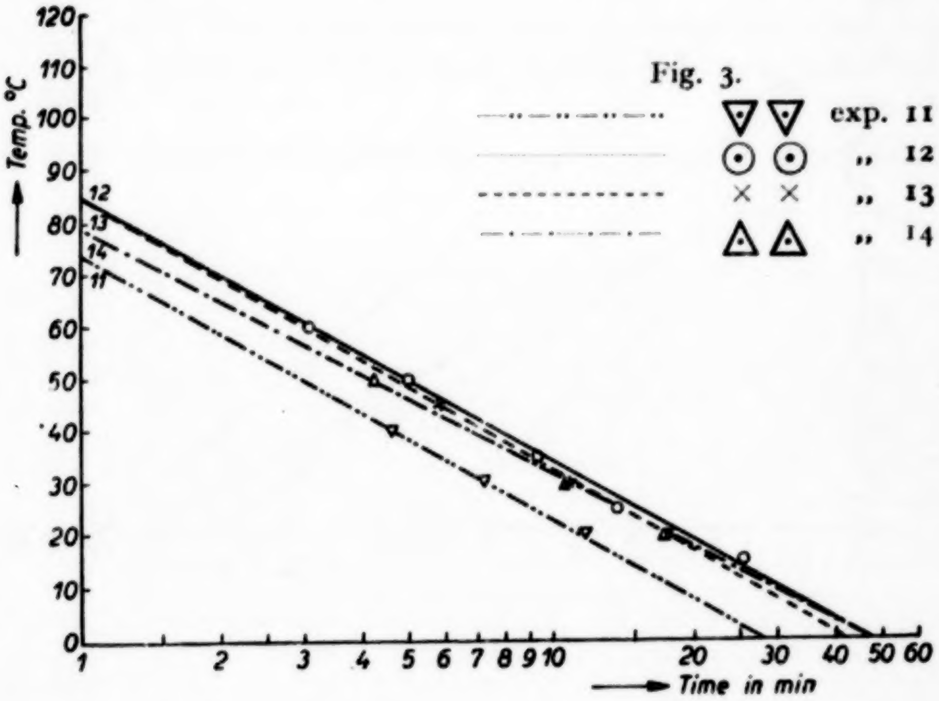

Fig. 3.

From an examination of these values it is seen that *k* is reasonably constant considering the bad definition of the experimental conditions. In the experiments 1-11 (12-14 will be discussed later) *k* is always between 0.013 and 0.021 except in nr. 2. The mean is 0.017, the standard deviation s = 0.003. As the *k* value of nr. 2 deviates 0.11 from the mean it is not used for further considerations.

If *k* is known it is theoretically possible to calculate the influence of number and weight of the crucibles on the values of T_0 and t_1. T_0 should vary proportionally to their heat capacity and therefore to their number and weight. Variations in t_1 may be derived from $t_1 = \frac{\log T_0}{k}$, showing that the cooling period is inversely proportional to the heat-transmission coefficient of the desiccator if its heat capacity remains unchanged. Examination of the experimental values shows that there is too much variation to conclude that this is quantitatively verified, although there is a trend in the expected direction (Table II).

Further, the recommended cooling periods of 25-45 minutes give rise to temperature differences which are seldom less than 5°C and often much more.

2. *Experiments on weighing*

Weighings were carried out with an analytical balance. On the right hand pan sufficient weights were placed so that after placing the warm crucible on the left hand pan equilibrium was expected roughly. The change of the rest-point with time (each rest-point determined from three readings) was noted, and from this the change of apparent weight with time was calculated. Noted were (Table III) the maximum difference from the final weight (Δ_m), the difference two minutes after the moment at which the crucibles had been placed on the pan (Δ_2) and the time necessary to obtain an apparent weight which differed not more than 0.1 mg from the final weight ($t_{0,1}$). The initial temperature of the crucibles was obtained on some occasions by placing them in a beaker with controlled temperature, but in most cases the weighings followed the experiments of the former paragraph, broken up after a certain time. In that case they are noted in Table III, with a W and the number of the corresponding cooling experiment.

TABLE III

Experiment	*Temperature difference*	*Type of crucible*	Δm	Δ_2	$t_{0,1}$	$\frac{\Delta m}{\Delta T}$	$\frac{\Delta_2}{\Delta T}$
1 W	$2^\circ.4$	A	0.3	0.2	5	0.13	0.08
2 W	$1^\circ.6$	B	0.3	0.1^3	5	0.19	0.08
3 W	$2^\circ.2$	B	0.4	0.3	8	0.18	0.14
4 W	$4^\circ.6$	A	0.6	0.5	7	0.13	0.11
5 W	$5^\circ.6$	A	—	0.7	8	—	0.13
6 W	$6^\circ.1$	B	0.7	0.4	8	0.11	0.07
7 W	$5^\circ.0$	A	0.8	0.7	10	0.16	0.14
15	$6^\circ.5$	B	0.8	0.8	13	0.12	0.12
16	$3^\circ.5$	A	0.7	0.3	6	0.20	0.08
17	$3^\circ.4$	B	0.6	0.4	6	0.18	0.12

From Table III it is seen that the maximum deviation in the apparent value is 0.16 mg/°C (s = 0.03). This deviation was found after about one minute. Because with the automatic balances now available it is possible to make weight readings about one minute after the object has been placed on the balance-pan, deviations from the right value of this magnitude may be obtained. After two minutes the deviation is slightly less (mean 0.11 mg/°C, s = 0.03). BLADE[1] found a mean maximum deviation of 0.19 mg/°C, when weighing crucibles not cooled in a desiccator, but artificially brought to temperatures different from the balance case.

CONCLUSIONS

Summarizing the figures of the former tables it is seen that the errors due to insufficient cooling periods may be serious; a review is given in Table IV.

TABLE IV

Cooling period	*Possible error in weighing*
20-66 min	0.8 mg
50-96 ,,	0.3 mg
73-119 ,,	0.16 mg

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[1] E. BLADE, *Ind. Eng. Chem., Anal. Ed.*, 12 (1940) 330.

This table shows that in unfavourable cases (the desiccator quite filled with crucibles) even after more than one hour of cooling an error of 0.8 mg may result, and that in order to be sure that the error due to a temperature difference of balance and crucible is not more than 0.16 mg a cooling period of 73 minutes is required, even when two crucibles are placed in a desiccator big enough for seven.

The required cooling period may be diminished by the following measures:

1. Cooling the crucible some time in air before placing it in the desiccator.
2. Placing few crucibles in the desiccator.
3. Placing the crucibles for some time in the balance-case before weighing. Of course this is not possible if the substance in the crucible is hygroscopic.

The influence of the change of relative vapour tension on the weight of the crucibles was proved to be not more than 0.1 mg.

4. The formula $t_1 = \frac{\log T_0}{k}$ shows that the cooling period is inversely proportional to the heat transmission k of the desiccator. With the material used at present it seems difficult to make this much better without increasing the fragility of the apparatus. Construction of desiccators of other materials might lead to improvement.

The author thanks Prof. Dr. W. van Tongeren for suggestions which led to the improvement of the manuscript.

SUMMARY

When porcelain crucibles are quickly weighed on automatic balances every degree of temperature difference between crucible and balance may give an error of about 0.16 mg. The cooling of ignited crucibles during the time recommended in several handbooks (25-45 minutes) may lead to final temperature differences of 10°C or more and errors of 2-3 mg. The change of temperature difference with time is logarithmic and from this the influence of the heat-transmission coefficient of the desiccator may be derived.

RÉSUMÉ

Lorsque des creusets de porcelaine sont rapidement pesés sur des balances automatiques, chaque degré de différence de température entre le creuset et la balance peut donner une erreur d'environ 0.16 mg. Le refroidissement des creusets calcinés pendant le temps recommandé dans plusieurs ouvrages (25-45 minutes) peut conduire à des différences de température de 10°C ou plus et à des erreurs de 2-3 mg. Le changement de différence de température avec le temps est logarithmique et l'influence du coefficient de transmission de chaleur du dessicateur peut en être déduite.

ZUSAMMENFASSUNG

Beim raschen Wägen von Porzellantiegeln auf automatischen Waagen kann jeder Grad Temperaturunterschied zwischen Tiegel und Waage einen Fehler von ungefähr 0.16 mg verursachen. Das Abkühlen von geglühten Tiegeln während der in verschiedenen Lehrbüchern empfohlenen Zeit (25-45 Minuten) kann zu Temperaturunterschieden von 10°C oder mehr und zu Fehlern von 2-3 mg führen. Die Änderung des Temperaturunterschiedes ist eine logarithmische Funktion der Zeit; hiervon kann der Einfluss des Wärmeleitungs-Koeffizienten des Exsikkators abgeleitet werden.

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THE THERMOLYSIS OF THE RARE EARTH AND OTHER METAL NITRATES

by

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In a recent study involving the determination of the solubilities of some rare earth and other metal nitrates in organic solvents[1,2], it was found that little was known concerning the thermal decomposition of these nitrates to their corresponding oxides. This information was desired because the organic solvent solutions of the metallic nitrates were evaporated and the resulting residues ignited and weighed as the metal oxides.

Previous investigations on the thermal decomposition of the hydrated rare earth nitrates were concerned mainly with the composition of the intermediate products formed and not the temperature limits for the appearance of the oxide levels[3,4,5]. As a result of this incomplete information, the hydrated nitrates of scandium, yttrium, uranium(VI), thorium, zirconium, lanthanum, cerium(III), praseodymium, neodymium and samarium were pyrolyzed on the thermobalance.

EXPERIMENTAL

Chemicals

The sources of the yttrium and rare earth compounds have been previously described[6]. Scandium oxide of 99.8% purity was obtained from A. D. Mackay & Co., New York, N.Y. Uranium(VI) nitrate hexahydrate, reagent grade, was obtained from Merck & Co., Rahway, N. J. Zirconyl nitrate pentahydrate, C.p., was obtained from the E. H. Sargent and Co., Chicago, Ill. Thorium nitrate tetrahydrate was obtained from the Lindsay Chemical Co., West Chicago, Ill. All other chemicals were of analytical reagent grade.

Preparation of the hydrated metal nitrates

For those metals not obtained in the form of the nitrates, the hydrated nitrates were prepared. The metal oxides were dissolved in a minimum volume of $6N$ HNO_3 and after evaporating to a small volume, were allowed to crystallize. The resulting crystals of the metal nitrates were then pyrolyzed on the thermobalance.

Thermobalance

The construction and operation of the thermobalance has previously been described[7]. Sample sizes ranged from 100-200 mg. The heating rate for all samples was 4.5°/min.

DISCUSSION

Rare earth nitrates

All of the rare earth nitrate hexahydrates decomposed in the same general manner except cerium(III). The water of hydration began to come off in the temperature range 30 to 50° with the formation of intermediate hydrates of varying stabilities until a horizontal was reached containing the anhydrous metal nitrate. The anhydrous metal nitrates then decomposed to give oxynitrates of the general formula, $MONO_3$, which subsequently decomposed to give the corresponding metal oxides. The thermolysis curves are shown in Fig. 1 with the minimum temperature limits for the oxide levels given in Table I.

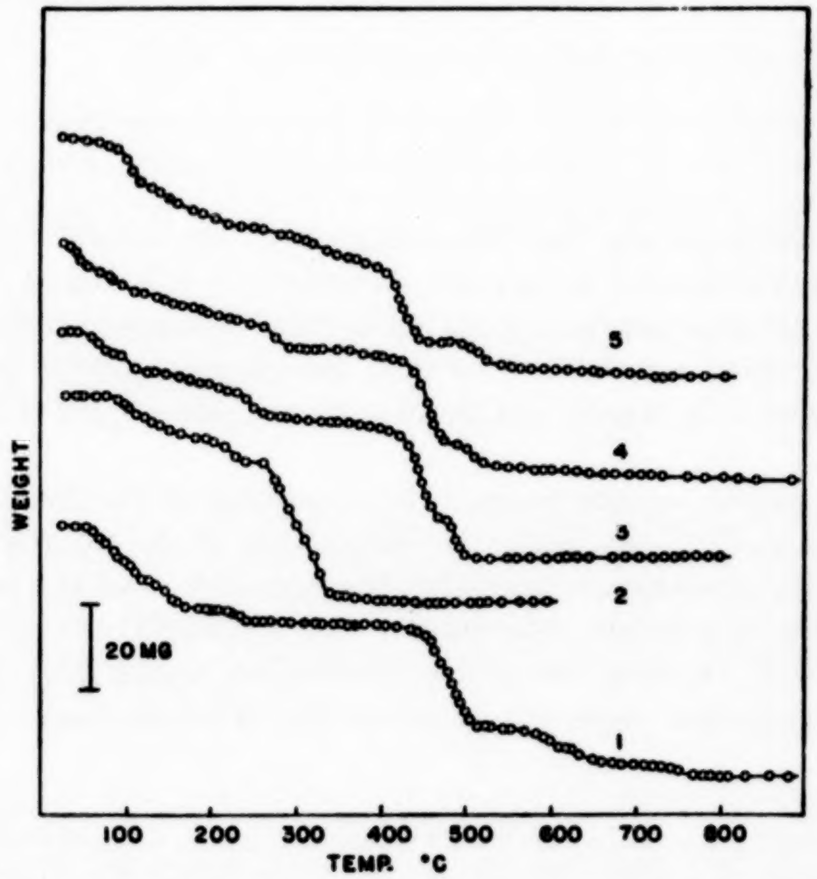

Fig. 1. The thermolysis curves of the rare earth nitrates

1. $La(NO_3)_3 \cdot 6H_2O$
2. $Ce(NO_3)_3 \cdot 6H_2O$
3. $Pr(NO_3)_3 \cdot 6H_2O$
4. $Nd(NO_3)_3 \cdot 6H_2O$
5. $Sm(NO_3)_3 \cdot 6H_2O$

Lanthanum nitrate hexahydrate. The hexahydrate began to lose water of hydration at 50° and gave inflections in the thermolysis curve at the pentahydrate and dihydrate compositions. However, no horizontals were observed because of the heating rate employed. A horizontal corresponding to the monohydrate began at 170° which lost water to form the anhydrous salt, $La(NO_3)_3$, at 240°. The anhydrous salt began to lose oxides of nitrogen at 420° resulting in a horizontal at 515° of the oxynitrate, $LaONO_3$. This began to decompose at 575° and resulted in the formation of La_2O_3 at 780°. The thermolysis of this compound shows that the anhydrous lanthanum nitrate can be prepared by heating the hydrated salt.

References p. 439.

TABLE I

MINIMUM OXIDE TEMPERATURE LIMITS FOR THE METAL NITRATES*

Metal nitrate	*Oxide*	*Temperature °C*
Lanthanum	La_2O_3	780
Cerium(III)	CeO_2	450
Praseodymium	Pr_6O_{11}	505
Neodymium	Nd_2O_3	830
Samarium	Sm_2O_3	750
Scandium	Sc_2O_3	510
Yttrium	Y_2O_3	480
Uranium	U_3O_8	550
Thorium	ThO_2	480
Zirconium	ZrO_2	575

* Heating rate of 4.5°/min

Cerium(III) nitrate hexahydrate. The thermolysis pattern of cerium(III) nitrate was different from those of the other rare earth metal nitrates. Instead, the decomposition pattern was similar to that of thorium nitrate. No intermediate hydrates were detected nor was $CeONO_3$ found in the thermolysis curve. The hexahydrate was stable up to 80° where it gradually lost water and finally oxides of nitrogen to give the CeO_2 horizontal beginning at 450°.

Praseodymium nitrate hexahydrate. The hexahydrate began to lose water at 50° but no well defined horizontals of intermediate hydrates were found. The loss of water resulted in a horizontal which began at 300° for the anhydrous $Pr(NO_3)_3$. The anhydrous nitrate began to lose oxides of nitrogen at 375° and gave a break in the curve at 470 to 480° corresponding to $PrONO_3$. The oxide, Pr_6O_{11}, appeared at 505°.

Neodymium nitrate hexahydrate. The hexahydrate began to lose water at room temperature. No intermediate hydrates were detected. The anhydrous $Nd(NO_3)_3$ was stable from 290 to 380°. This is perhaps the first time that the anhydrous nitrate was prepared by thermal decomposition of the hydrated salt at atmospheric pressure. SELWOOD[9] previously prepared the anhydrous nitrate by heating the hexahydrate under several mm of Hg pressure. The anhydrous nitrate began to lose oxides of nitrogen at 380° and gave a break in the curve at about 475° which corresponded to the oxynitrate, $NdONO_3$. No well defined horizontal was obtained due perhaps to the excessive heating rate employed. A horizontal corresponding to the oxide, Nd_2O_3, was obtained beginning at 830°. This was the highest minimum oxide temperature obtained from all of the compounds studied. This is not surprising however because DUVAL[8] found that the oxide level in neodymium oxalate did not appear until 813°.

Samarium nitrate hexahydrate. The hexahydrate was stable to about 50° where it began to lose water. No intermediate hydrate horizontals were detected nor was there a horizontal corresponding to the anhydrous $Sm(NO_3)_3$. An oxynitrate, $SmONO_3$, did appear in a horizontal in the temperature range of 450 to 490°. The oxide horizontal of Sm_2O_3 appeared at 750°.

Yttrium and scandium nitrates. The thermolysis curves are shown in Fig. 2 with the temperature limits for the oxide levels given in Table I. Yttrium nitrate hexahydrate began to lose water at room temperature but intermediate hydrate horizontals were not detected. A horizontal corresponding to the anhydrous $Y(NO_3)_3$ was not detected either. A short horizontal at 440 to 475° corresponding to the oxynitrate, $YONO_3$, was found. The oxide horizontal began at 660°. In many respects the thermolysis curve of this compound was similar to that of samarium nitrate.

Scandium nitrate hexahydrate decomposed to give horizontals which did not correspond to the anhydrous $Sc(NO_3)_3$ or the oxynitrate, $ScONO_3$. The horizontals obtained did not correspond to any stoichiometric compounds and were probably mixtures. The oxide horizontal appeared at 510°.

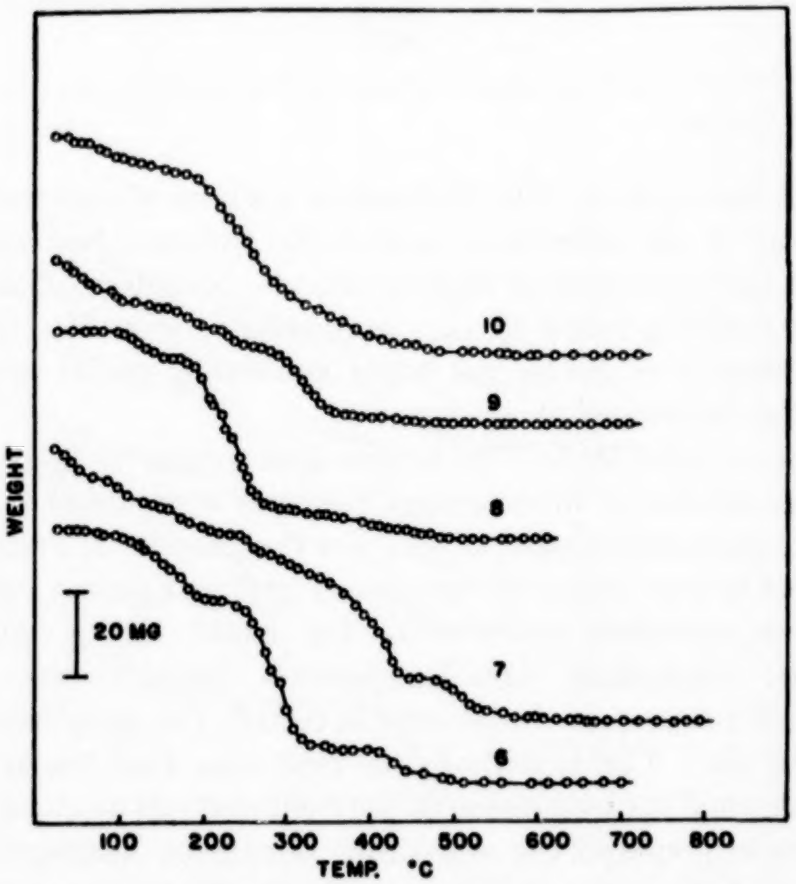

Fig. 2. The thermolysis curves of the metal nitrates.
6. $Sc(NO_3)_3 \cdot 6H_2O$
7. $Y(NO_3)_3 \cdot 6H_2O$
8. $Th(NO_3)_4 \cdot 4H_2O$
9. $UO_2(NO_3)_2 \cdot 6H_2O$
10. $ZrO(NO_3)_2 \cdot 5H_2O$

Thorium, zirconyl and uranium(VI) nitrates

The thermolysis curves are shown in Fig. 2 with the minimum oxide temperatures given in Table I. The thermolysis curves of thorium and zirconyl nitrates were similar in appearance. In neither case was a horizontal obtained which corresponded to the anhydrous metal nitrates. The ThO_2 horizontal began at 480° while that of ZrO_2 began at 575°. The oxide horizontals for these two compounds appeared at about the same temperatures as that of CeO_2.

Uranium(VI) nitrate hexahydrate began to lose water at 30° and gave a short horizontal which corresponded to anhydrous $UO_2(NO_3)_2$ at 200 to 220°. The oxide, U_3O_8, appeared at 550°.

References p. 439.

SUMMARY

The thermolysis curves of the nitrates of lanthanum, cerium(III), praseodymium, neodymium, samarium, yttrium, scandium, thorium, uranium(VI) and zirconium were determined. The oxide levels were obtained in the temperature range of 450-830°.

RÉSUMÉ

Les courbes de thermolyse des nitrates de lanthane, cérium(III), praséodyme, néodyme, samarium, yttrium, scandium, thorium, uranium(VI) et zirconium ont été établies. Les paliers des oxydes sont atteints entre 450° et 830°.

ZUSAMMENFASSUNG

Die Thermolyse-Kurven der Nitrate von Lanthan, Cer(III), Praseodym, Neodym, Samarium, Yttrium, Scandium, Thorium, Uran(VI) und Zirkonium wurden bestimmt. Die Oxydstufen wurden zwischen 450 und 830° erreicht.

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DETERMINATION OF MICRO-AMOUNTS OF BORON IN URANIUM METAL AND IN URANYL CHLORIDE SOLUTIONS

by

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Boron, if present with polyvalent ions in aqueous solution, is usually first separated by alcohol-distillation[1], then determined by suitable means. Anderson and Motta[2] used the alcohol-distillation method for the determination of boron in uranium. Russell[3], in a comprehensive survey of the literature for the determination of boron in trace quantities, noted that the boron recoveries were not as complete as might be desired (repeated alcohol-distillations are required), but that the results were indicative of the amounts present.

Silverman and Trego[4] made a basic study of the effects of reagents on micro-amounts of boron and found that an alcohol-distillation was not necessary using the curcumin-acetone solution method. This direct determination procedure is now applied to the determination of micro-amounts of boron in uranium metal or in uranyl chloride solution. The presence of uranium necessitates changes in the amounts of the necessary reagents which permit the formation of an acetone-soluble uranium oxalate.

EXPERIMENTAL

Reagents

The reagents were described in the previous paper[4]. In addition:

Uranium as uranyl chloride. Dissolve 13.6 grams of uranium trioxide (83.2 per cent U) in 10 ml hydrochloric acid. Dilute to 2 liters with water. One ml equals 5 mg of uranium.

Paper pulp in acetone solution. Crush squares of filter paper pulp manually and shake well in an acetone solution.

Procedure

Uranyl chloride solutions

Choose an aliquot estimated to contain 25, 50, or 100 mg of uranium. Transfer the sample to a 100-ml porcelain crucible, add one drop of phenolphthalein solution, neutralize with a 10 per cent sodium carbonate solution, 1 ml at a time, and add an excess of 1 ml. (The uranium is now in solution as uranyl carbonate complex.)

Evaporate the solution to dryness in a 110-120°C oven, then cool. Use a small glass rod as a stirring rod and titrate with a (1 to 4) hydrochloric acid solution until the red phenolphthalein solution turns to a bright yellow, (not orange) and add 0.1 ml in excess. Add 10 per cent oxalic acid solution in the following ratio: 10 ml for 25 mg of uranium, 15 ml for 50 mg of uranium and 25 ml for 100 mg of uranium (see Fig. 1). Add 3 ml of curcumin and carefully swirl the solution in the crucible.

Place the crucible in a 55°C oven (or water bath) and evaporate to dryness. (This is a critical point in the procedure. The drying should be completed[3] in an oven. Under-drying results in cloudy solutions which are difficult to filter. Over-drying vitiates the color. All traces of moisture must have disappeared before the sample is considered dried. Crystals frequently appear if the sample has been dried slowly. The crucible must be removed from the oven, not more than 30 minutes after the residue appears to be moisture-free. The time of drying is dependent on the amount of solids present and the water contained in the hydrochloric acid solution.)

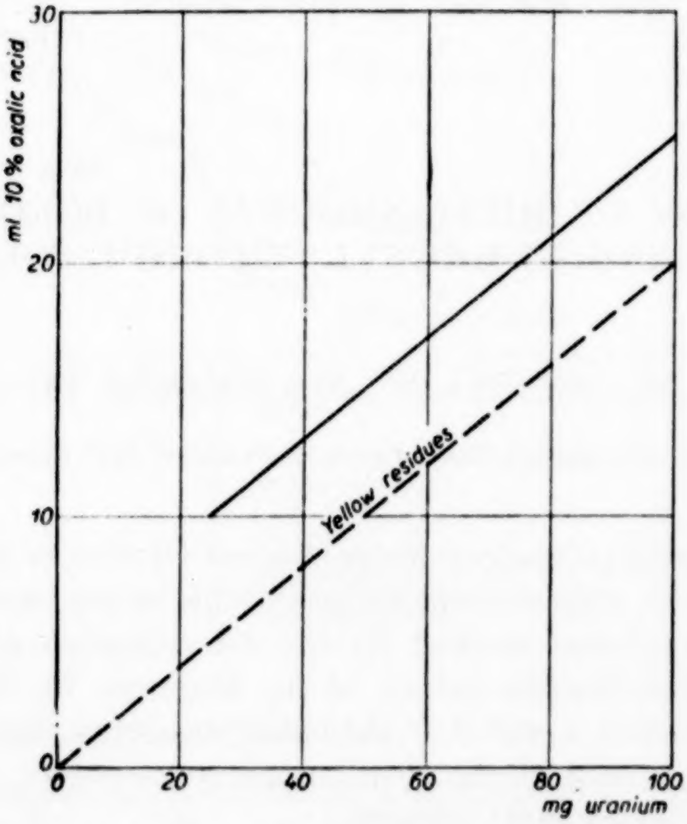

Fig. 1. ml oxalic acid required per mg of uranium.

Cool the crucible and wash down the walls with a minimum of acetone. Fill a 9-cm filter paper with paper pulp (suspended in acetone) and wash and drain several times. Filter the red boron solution. The pulp should be kept moist.

Dilute the filtrate to volume[4], mix, and read on a Beckman spectrophotometer at 535 mμ and a slit width of 0.04 to 0.07. Use a prepared boron-free uranyl chloride solution as reference solution.

References p. 445.

Uranium metal (100-mg aliquot-samples)

Transfer 500 mg of uranium metal to a 200-ml Erlenmeyer flask. Fit the flask with a one-hole stopper and a 40 to 50-cm glass tube, to be used as a reflux condenser. Add 1 ml of concentrated hydrochloric acid solution and 1 to 2 ml of 30 per cent hydrogen peroxide. When rapid action ceases, place the flask and condenser on a warm plate (40 to 60°C) and warm until the decomposition of the hydrogen peroxide is complete. Cool. Add an equal amount of water.

Filter through a 9-cm paper into a 100-ml volumetric flask, and wash with water. Reserve the paper and contents for further analysis (insoluble borides) and treat filtrate as described below. Dilute the filtrate to the mark.

Preparation of a reference-blank solution

Transfer 2 aliquots of 20 ml each (100 mg) to 50-ml Erlenmeyer flasks. Add 5 ml of concentrated hydrochloric acid and rapidly evaporate to dryness, but do not bake. Add 5 ml of concentrated hydrochloric acid solution, and re-evaporate. Repeat this evaporation 3 times more. At this point these aliquots are certain to be boron-free and are to be used as reference solutions (see below). Transfer the solutions to 100-ml crucibles using minimum amounts of water. Add phenolphthalein, neutralize with sodium carbonate solution and proceed as described under uranyl chloride solutions. These are the reference-blank solutions, as described under uranyl chloride solutions.

Test samples

Transfer 2 aliquots of 20 ml each (100 mg) to 100-ml crucibles, add phenolphthalein and sodium carbonate solution and proceed as described under uranyl chloride solutions. These are the test solutions, in duplicate. They are to be read against the boron-free reference-blank solutions.

Obtain readings at 535 mμ, and calculate the soluble boron content from the standard curve.

Insoluble borides

Dry the paper in a small platinum crucible, and ignite at 850°C. Cool. Add 0.2 gram of anhydrous sodium carbonate, cover the crucible, and fuse for 10-15 minutes. Cool. Scrape down the cover and wall of the crucible, add just enough water to dissolve the residue, add one drop of phenolphthalein and evaporate to dryness in a 100-110°C oven. Titrate with (1 to 4) hydrochloric acid until the red phenolphthalein is colorless and add 0.5 ml in excess. Add 0.5 ml of 5 per cent oxalic acid solution. Evaporate the solution to dryness and proceed to determine boron, as a uranium-free sample[4]. Calculate for an original sample-weight of 500 mg.

Preparation of boron-free uranyl chloride for the standard curve

Evaporate 25, 50 or 100-mg aliquots of uranyl chloride 5 times with 5 ml of concentrated hydrochloric acid, as described above. Take up in water, add 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 microgram of boron (as boric acid) to the respective crucibles and proceed as above. Plot the standard curve, noting that 0.1 and 0.2 microgram of boron are of the same intensities (Fig. 7).

RESULTS AND DISCUSSION

Uranyl chloride solutions — 25 mg, 50 mg, and 100 mg uranium

With constant uranium content and curcumin solution, the reagent variables to be studied were the oxalic acid and the amount of excess hydrochloric acid. The optimum concentration of oxalic acid in the presence of 25 mg of uranium is in the neighborhood of 10 ml of 10 per cent oxalic acid. Figs. 2, 3, and 4, respectively, show that the optimum amount of excess hydrochloric acid (1 to 4) is 0.1 to 0.2 ml when using 25 mg of uranium and 10 ml of 10 per cent oxalic acid.

In the 50-mg uranium solution, 10 ml of 10 per cent oxalic acid solution are insufficient. The uranium is, in part, left as a yellow residue (Fig. 1). Fig. 5 shows that the optimum amount is about 15 ml of 10 per cent oxalic solution, and that higher amounts are deleterious.

In the 100-mg uranium solutions, 25 ml of 10 per cent oxalic acid solution is the most favored concentration (Fig. 6).

Fig. 7 shows that the absorbance for 0.0 microgram of boron is nearly equal to that of 0.2 microgram, but 0.25 microgram of boron showed an appreciable difference in absorbance. For this reason the lower limit of determination is set at 0.3 microgram of boron per 100 mg uranium (3 p.p.m.). The range lies from 0.3 to 50 micrograms of boron per 25 ml volume.

The advantage of this procedure for the determination of boron in uranium is the elimination of the repeated alcohol-distillations[3], with subsequent colorimetric determination. The study has shown that a specific amount of oxalic acid, enough to completely complex the uranium, along with a slight decrease in the amount of hydrochloric acid are the only necessary changes in the procedure when uranium is present in aqueous solution.

An extra precaution is advisable when determining these smaller quantities of boron. Since unknown interfering impurities may be found in the test samples of uranium metal, oxides and salts, the procedure is written so that the uranium of the test sample is included in the reference solution for the absorbance measurement. (It was shown above that the last detectable traces of boron may be volatilized [hydrochloric acid method] from uranyl chloride solution by repeated evaporations.) In this manner, metal chlorides which absorb at 535 mμ, in acetone solutions, will not lead to false absorbance readings.

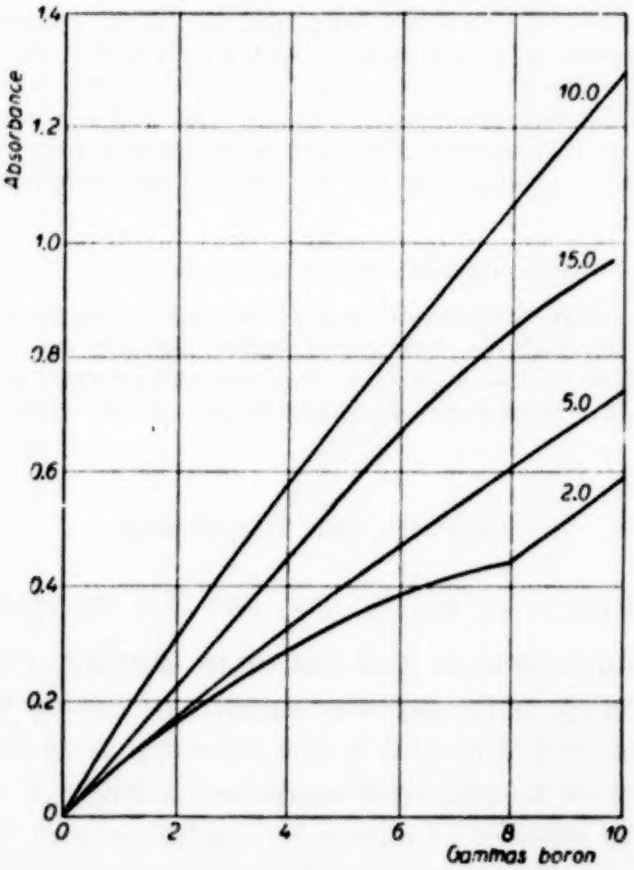

Fig. 2. ml of 10 per cent oxalic acid for 25 mg uranium.

25 mg uranium
1.0 ml 10% Na_2CO_3
0.5 ml excess (1 : 4) HCl
3.0 ml curcumin

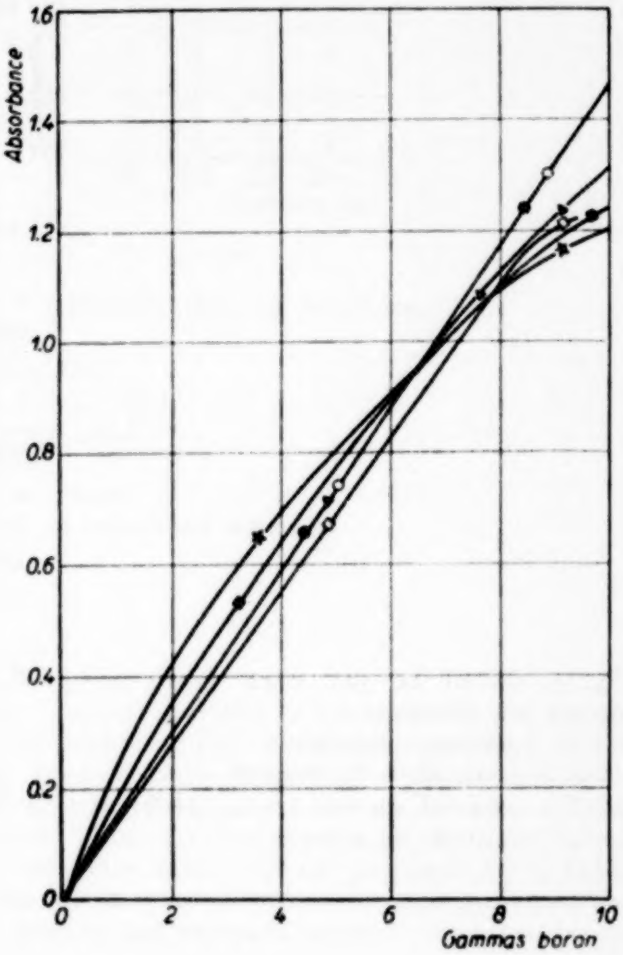

Fig. 3. ml of excess hydrochloric acid for 25 mg uranium.

25 mg uranium
1.0 ml 10% Na_2CO_3
10 ml 10% $H_2C_2O_4$
3.0 ml curcumin
Code: ml excess (1 : 4) HCl
◐ 0.0
● 0.1
▲ 0.2
○ 0.3
⬟ 0.5
▪ 1.0

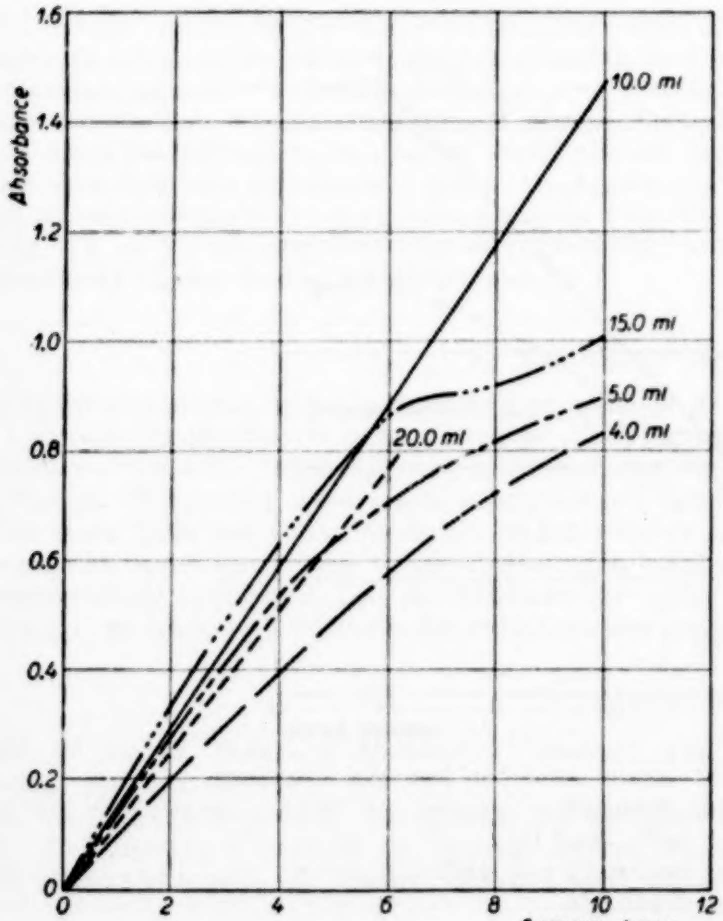

Fig. 4. ml of 10 per cent oxalic acid for 25 mg uranium.

25 mg uranium
1.0 ml 10% Na_2CO_3
0.1 ml excess (1 : 4) HCl
3.0 ml curcumin

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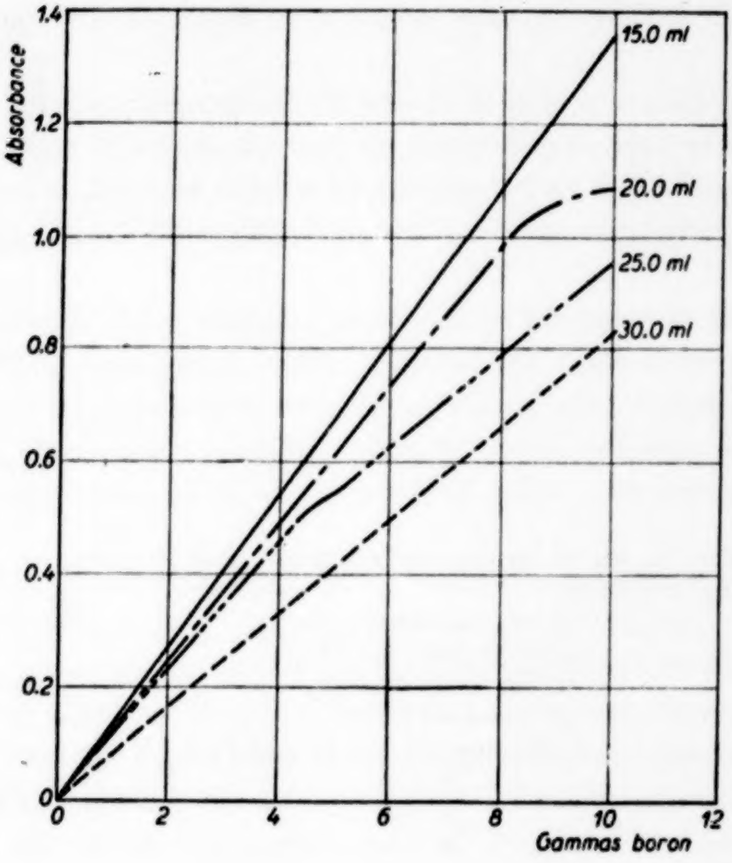


Fig. 5. ml of 10 per cent oxalic acid for 50 mg uranium.
50 mg uranium
2.0 ml 10% Na_2CO_3
0.1 ml excess (1 : 4) HCl
3.0 ml curcumin

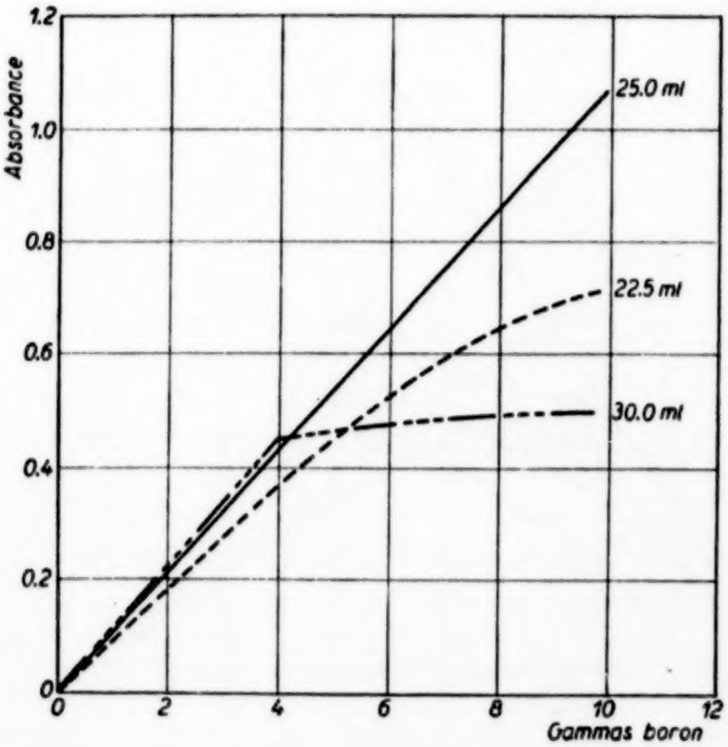
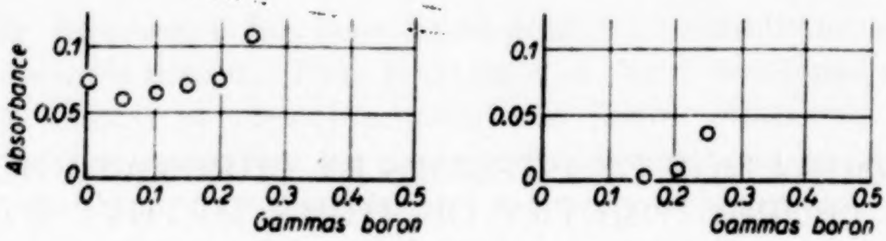


Fig. 6. ml of 10 per cent oxalic acid for 100 mg uranium.
100 mg uranium
3.0 ml 10% Na_2CO_3
0.1 ml excess (1 : 4) HCl
3.0 ml curcumin

References p. 445.



(a) (b)

Fig. 7. Limits for determination of boron in 100 mg uranium.
100 mg uranium
3.0 ml 10% Na_2CO_3
0.1 ml excess (1 : 4) HCl
25 ml 10% oxalic acid
3.0 ml curcumin
(a) Acetone as reference solution.
(b) Reagents and uranium as reference solution.

SUMMARY

The direct colorimetric determination of boron (curcumin-oxalic acid method) in uranyl chloride solution is possible, without prior removal of uranium. The interference ascribed to the presence of uranium lies in the fact that uranium preferentially combines with the available oxalic acid. If, therefore, suitable excess of oxalic acid is added, the uranium forms a soluble uranium-oxalate complex which need not be removed. Thus, no preliminary alcohol-distillation is required. Special boron-free spectrophotometric reference solutions are prepared by a rapid hydrochloric acid-volatilization method. Acid-soluble boron, 3 to 50 p.p.m., is determined in the presence of 100 mg of uranium. Insoluble boron is determined separately after carbonate fusion of the acid-insoluble portion.

This report is based on studies performed for the Atomic Energy Commission under Contract AT-11-1-GEN-8.

RÉSUMÉ

Le dosage colorimétrique direct du bore (curcumin-acide oxalique) dans une solution de chlorure d'uranyle est possible, sans séparation préalable de l'uranium. La perturbation de l'uranium est due au fait qu'il se combine de préférence avec l'acide oxalique disponible. Par conséquent, si un excès convenable d'acide oxalique est ajouté, l'uranium forme un complexe uranium-oxalate qu'il n'est pas nécessaire d'éliminer. Ainsi aucune distillation préliminaire d'alcool n'est nécessaire. Des solutions de référence spectrophotométriques spéciales exemptes de bore sont préparées par une méthode de volatilisation rapide à l'acide chlorhydrique. Le bore soluble en solution acide, 3 à 50 p.p.m., peut être dosé en présence de 100 mg d'uranium. Le bore insoluble est dosé séparément, après fusion au carbonate.

ZUSAMMENFASSUNG

Die direkte kolorimetrische Bestimmung von Bor (nach der Kurkumagelb-Oxalsäure-Methode) in Uranylchloridlösung ist ohne vorherige Abtrennung des Urans möglich. Die dem Uran zugeschriebene störende Wirkung beruht darauf, dass dieses sich mit der verfügbaren Oxalsäure verbindet. Wenn man aber einen genügenden Überschuss an Oxalsäure zufügt, so bildet das Uran einen löslichen Uran-Oxalat-Komplex welcher nicht entfernt werden muss. Spezielle borfreie spektrophotometrische Vergleichslösungen werden mit Hilfe einer raschen HCl-Verflüchtigungsmethode hergestellt. Das säurelösliche Bor (3 bis 50 Teile pro Million) wird in Gegenwart von 100 mg Uran bestimmt, während das unlösliche Bor separat, nach Carbonatschmelze bestimmt wird.

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THE DETERMINATION OF PHENOLS BY CHROMATOGRAPHY AND SPECTROPHOTOMETRY OF THEIR METHYL ETHERS

I. ULTRAVIOLET ABSORPTION SPECTRA OF METHYL ARYL ETHERS IN CYCLOHEXANE

by

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INTRODUCTION

Recently the determination of phenols has become of increasing importance in connection with industrial effluent control, river pollution and the examination of combustion products. In this latter connection it became necessary to devise an analytical method to determine microgram amounts of phenols in the presence of each other and considerably larger amounts of other compounds. The new method, of which a preliminary account[1] has already been published, has a number of advantages over other analytical techniques in general use, and has been applied successfully to combustion products.

The principle of the method is to convert the phenols quantitatively into their methyl ethers by dimethyl sulphate in the presence of alkali and to separate the methyl ethers in cyclohexane solution by chromatography on alumina columns. The detection and determination of the ethers in successive eluates is effected by the recognition of characteristic absorption peaks in the ultra-violet spectra and the measurement of peak heights. The spectra of the methyl aryl ethers are especially suitable as they are all characterized by absorption peaks which, in cases of the phenols of the polycyclic hydrocarbons are very similar to those of the corresponding hydrocarbons[2]. Theoretical aspects of these characteristic spectra have been discussed by BRAUDE[3]. The use of reduction and methylation has already proved to be of considerable value in determining the oxidation products of certain polycyclic hydrocarbons[4], which, although frequently are found to be quinones, may contain phenols. In the present study, methods for the simpler and more commonly occurring phenols have been devised.

Review of other methods for the determination of phenols

Most methods for the determination of phenols do not distinguish between individual compounds of this class; the more sensitive of these rely upon colorimetric techniques. It thus transpires that for the majority of determinations it has been customary to quote the results in terms of phenol (hydroxybenzene) and, since this compound with its simple homologues the cresols forms the major proportion of the phenolic content of effluents, tar acids and combustion products, the procedure has been satisfactory.

More recently, however, it has been found desirable to obtain an estimate of the individual compounds present. Thus HASLAM *et al.* have developed a method[5] for phenol and the cresols in phenol-formaldehyde resins. ASHMORE AND SAVAGE[6] have relied upon the separation by paper strip chromatography of the azo dyes produced from the same four phenols, and a similar technique has been used for determination of the phenols in cigarette smoke[7]. Recently the phenolic components of "tar acids" have been separated by alumina chromatography and determined by spectrophotometry[8]. The present method, employing the methyl ethers of the phenols, is not subject to losses by oxidation during chromatography and has advantages over all the others mentioned in that individual compounds may be determined in mixtures on a microchemical scale with good accuracy. Further the process of methylation in alkaline solutions eliminates all other compounds than phenolic methoxycompounds.

EXPERIMENTAL

Preparation of methyl aryl ethers

Although some phenols are available commercially in a state of high purity, others are much less pure and frequently contain considerable quantities of isomeric or homologous phenols. The phenols used in this investigation were prepared from the purest commercially available products by distillation.

The purity was checked by measurement of melting points and boiling points and examination of the spectra of the methyl ethers; purification was repeated until these determinations gave constant values.

The methyl ethers were all prepared by dissolving the phenol in sodium hydroxide solution, adding diethyl sulphate in excess of the calculated amount and shaking vigorously. The whole was then boiled under reflux to destroy the excess of dimethyl sulphate with additional sodium hydroxide if necessary.

The methyl compounds were then separated by extraction with diethyl ether, drying and fractionally distilling. The methylated xylenols were purified by alumina chromatography. Table I shows the physical constants of the various phenols and their methyl ethers prepared for this investigation.

TABLE I

PHYSICAL CONSTANTS OF PHENOLS AND CORRESPONDING METHYL ETHERS

Phenol	*M.Pt.*	*B.Pt.*	*Ether B.Pt.*
Phenol	41	**182**	**155**
o-Cresol	30	**191**	**171**
m-Cresol	12	**203**	**177**
p-Cresol	**35**	**203**	**176**
2:3-Xylenol	**75**	**218**	**199 (29)**
2:4-Xylenol	26	**211**	**192**
2:5-Xylenol	**74.5**	**211**	**194**
2:6-Xylenol	**49**	**212**	**182**
3:4-Xylenol	**65**	**225**	**204**
3:5-Xylenol	**68**	**219**	**193**
Catechol	**105**	**245**	**206**
Resorcinol	**110**	**277**	**214**
Quinol	**170.5**	286	212 **(55)**
Guaiacol	**28.5**	**205**	206
1-Naphthol	**94**	280	**266**
2-Naphthol	**122**	286	**274 (72)**

Notes: Constants in heavy type were used as criteria of purity; values in brackets are melting points of the ethers.

Determination of ultra violet absorption spectra

Cyclohexane was chosen for these determinations because it is a good solvent for a large number of compounds, especially those of higher molecular weight found in combustion products. Also it has small ultra violet absorption in the range where the various solutes under investigation absorb strongly.

It was prepared from the purest commercially available redistilled material by passing through a column (150 × 5 cm) of silica gel* freshly activated by heating to 300°C. This adequately removed the small traces of benzene present. The purity was checked spectrophotometrically.

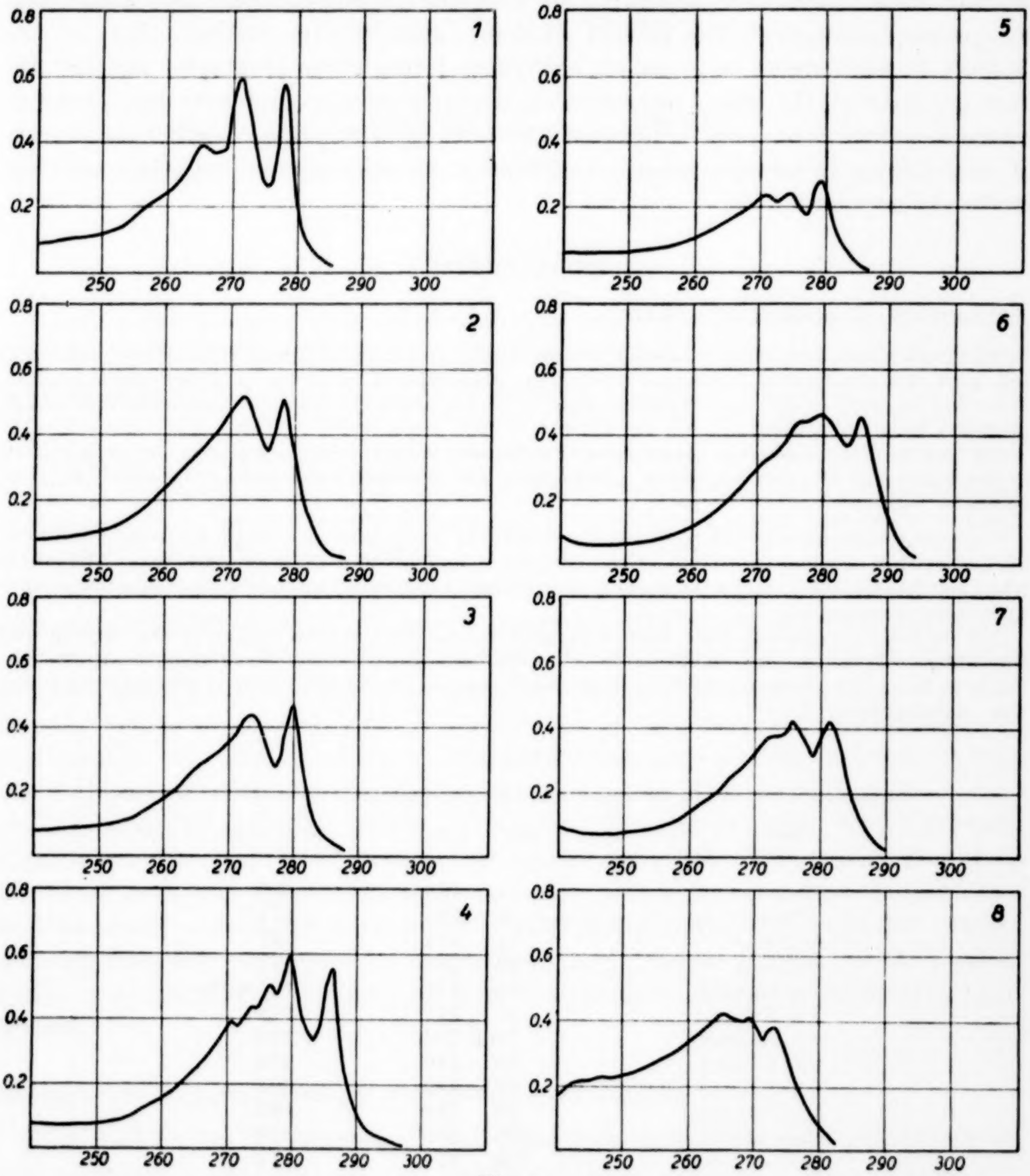

Fig. 1

1. Anisole 29.2 μg/ml.
2. *o*-Cresyl methyl ether 30.4 μg/ml.
3. *m*-Cresyl methyl ether 28.6 μg/ml.
4. *p*-Cresyl methyl ether 30.2 μg/ml.
5. 2:3-Xylenyl methyl ether 22.2 μg/ml.
6. 2:4-Xylenyl methyl ether 29.0 μg/ml.
7. 2:5-Xylenyl methyl ether 26.8 μg/ml.
8. 2:6-Xylenyl methyl ether 162.5 μg/ml.

Note: Optical densities are plotted vertically and wavelengths in millimicrons horizontally.

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* Sorbosil AP, Joseph Crosfield & Sons Ltd., Warrington, England.

Preliminary experiments showed that for concentrations of ethers up to 25 mg/l Beer's law holds accurately. Solution of this strength were prepared therefore by accurate weighing of the pure compounds on a micro-balance and making up to the required volume in standardized volumetric flasks. The S.P. 500 ultra violet spectrophotometer with matched silica cells was used at a constant slit width of 0.3 mm. The wave length scale was calibrated with reference to the hydrogen lines at 4861 Å and 6536 Å.

Generally readings were taken at intervals of 2 mμ, but at or near absorption peaks readings were made to 0.1 mμ. In the absorption curves reproduced in Figures 1 and 2 optical densities are plotted vertically.

In Table II, the wavelengths of all characteristic peaks of each compound are tabulated for easy reference. All determinations were repeated and the values confirmed.

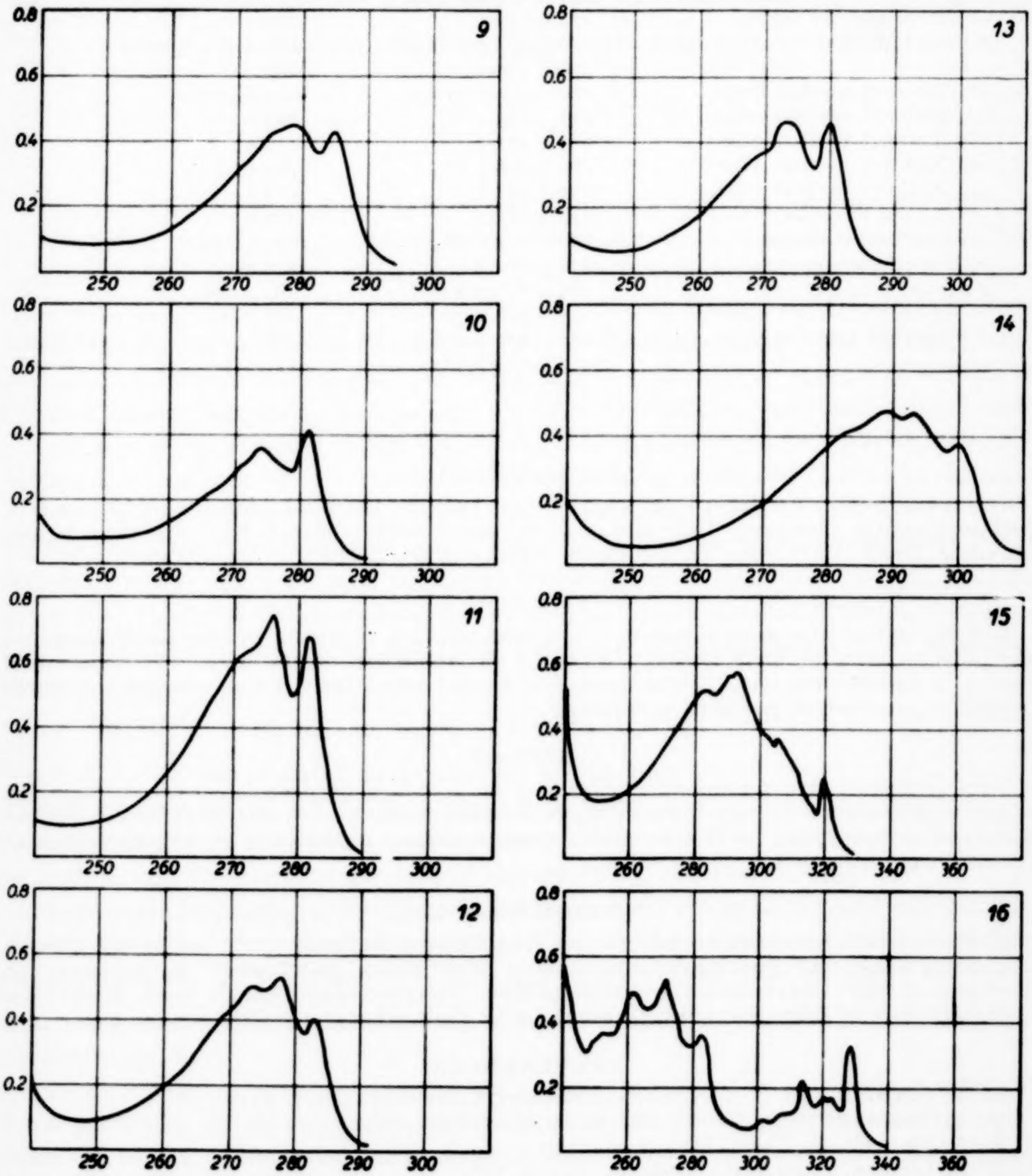

Fig. 2

9. 3:4-Xylenyl methyl ether	30.4 μg/ml.
10. 3:5-Xylenyl methyl ether	31.4 μg/ml.
11. Quaiacol	28.3 μg/ml.
12. *o*-Dimethoxybenzene	26.8 μg/ml.
13. *m*-Dimethoxybenzene	27.5 μg/ml.
14. *p*-Dimethoxybenzene	19.4 μg/ml.
15. 1-Naphthyl methyl ether	28.0 μg/ml.
16. 2-Naphthyl methyl ether	17.2 μg/ml.

Note: Optical densities are plotted vertically and wavelengths in millimicrons horizontally.

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In the further parts of this series analytical procedures will be described with their application to combustion products.

TABLE II

WAVELENGTHS OF THE MAIN MAXIMA AND MINIMA USED FOR IDENTIFICATION OF METHOXY HYDROCARBONS

Ether	*Maxima (mμ)*	*Minima (mμ)*
Anisole	265.0,271.3,278.0	267.0,275.5
o-Cresyl methyl ether	271.1,278.0	275.7
m-Cresyl methyl ether	272.9,279.7	277.1
p-Cresyl methyl ether	270.5,273.7,276.4 279.5,286.0	271.5,274.3,277.5 283.5
2:3-Xylenyl methyl ether	270.5,274.0,278.5	272.0,277.0
2:4-Xylenyl methyl ether	279.5,285.4	283.0
2:5-Xylenyl methyl ether	275.5,281.4	279.0
2:6-Xylenyl methyl ether	264.5,268.5,273.0	267.0,271.2
3:4-Xylenyl methyl ether	278.8,284.7	282.5
3:5-Xylenyl methyl ether	278.5,283.5	281.0
o-Dimethoxy-benzene	273.5,277.6,283.0	275.3,281.5
m-Dimethoxy-benzene	272.5,280.0	278.0
p-Dimethoxy-benzene	289.0,293.0,300.0	291.5,298.0
1-Naphthyl methyl ether	293.0,306.0,320.0	286.0,304.5,317.5
2-Naphthyl methyl ether	282.0,300.0,308.0 313.0,320.0,322.0 327.5	296.0,302.5,309.5,316.5 321.0,324.5

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SUMMARY

In this, the first of a series of papers on the determination of phenols by chromatography and spectrophotometry of their methyl ethers, the determination of the ultra-violet absorption spectra in cyclohexane solution of a number of methyl ethers derived from phenols commonly present in combustion products is described.

RÉSUMÉ

Dans ce premier article d'une série de travaux sur le dosage des phénols par chromatographie et spectrophotométrie de leurs éthers méthylés, les auteurs décrivent la détermination des spectres d'absorption dans l'ultra-violet d'un certain nombre d'éthers méthylés de phénols généralement présents dans les produits de combustion.

ZUSAMMENFASSUNG

In dieser Arbeit, der ersten einer Reihe von Arbeiten über die Bestimmung von Phenolen durch Chromatographie und Spektrophotometrie ihrer Methyläther, beschreiben die Verfasser die Bestimmung der Ultraviolett-Absorptionsspektren (in Cyclohexanlösung), einer Reihe von Methyläthern von Phenolen, welche regelmässig in Verbrennungsprodukten vorkommen.

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MULTIPLE DEVELOPMENT IN STRIP AND CIRCULAR CHROMATOGRAPHY

by

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In paper chromatography it is a common practice to have recourse to 'multiple development' when a single development fails to effect the desired separations. The number of developments, necessary to give the maximum separation, has been theoretically derived by JEANES *et al.*[1]. Some simpler conditions are deduced here which will help to decide whether, after one development, subsequent developments should be followed. As the multiple development technique is especially helpful in circular chromatography, the validity of these conditions has been tested here.

Let the two constituents of a mixture, subjected to paper chromatography, have R_F values, R_{F_1} and R_{F_2} ($R_{F_2} > R_{F_1}$). If the solvent front is allowed to travel a distance D from the starting point of the mixture, the distances d_1 and d_2, travelled respectively by the two constituents will be $R_{F_1}D$ and $R_{F_2}D$. In the next development if the solvent front is again allowed to travel the distance D from the original starting point then the total distances travelled d_1' and d_2' by the two constituents should be $\{d_1 + R_{F_1}(D\text{-}d_1)\}$ and $\{d_2 + R_{F_2}(D\text{-}d_2)\}$ respectively, from which it can be shown that

$$(d_2'-d_1') - (d_2-d_1) = (d_2-d_1)\ \{\ 1-(R_{F_1} + R_{F_2})\ \}$$

Since $d_2 > d_1$, the distance of separation of the two

1) will increase in the second development, if $(R_{F_1} + R_{F_2}) < 1$.
2) will decrease in the second development, if $(R_{F_1} + R_{F_2}) > 1$.
3) will remain the same in the second development, if $(R_{F_1} + R_{F_2}) = 1$.

In circular chromatography it has been shown both theoretically and experimentally[2,3,4] that the R_F value of a substance equals the square root of that in strip chromatography. Substituting $\sqrt{\frac{d_1}{D}}$ and $\sqrt{\frac{d_2}{D}}$ for R_{F_1} and R_{F_2} it would be found that the generalizations made for strip chromatography should also hold for circular chromatography.

The above deductions are made on the assumption that the R_F value is constant for a particular substance and is independent of the distance of the starting point from the source of the developing solvent which may not be so. Nevertheless, it will be clear from the experimental data given subsequently that the above generalizations hold fairly well.

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EXPERIMENTAL

Strip chromatography

0.5% solutions of the following amino acids were used: aspartic acid, glutamic acid, serine, glycine, alanine, threonine, valine and proline. 5-10 μl of the solutions were spotted at a point 7 cm away from the edge of a Whatman's No. 1 filter paper and developed in the descending way.

Tables I and II record the distances travelled by some amino acids (applied originally in a state of mixture) in successive stages of development in phenol-water and butanol-acetic acid-water (4:1:1), respectively. The figures within the brackets indicate the R_F values at each stage. The R_F value at each stage is calculated from the distances travelled by the spot and the solvent front from the position of the spot in the previous development.

TABLE I

DISTANCES TRAVELLED AND R_F VALUES FOUND DURING MULTIPLE DEVELOPMENT IN STRIP CHROMATOGRAPHY WITH WATER-SATURATED PHENOL AS THE DEVELOPING SOLVENT.
(d_1, d_2, d_3, d_4 are distances travelled in cm during first, second, third and fourth developments; R_F values are recorded in parentheses.)

	d_1	d_2	d_3	d_4
I. Distance travelled by solvent front in each case 35.0 cm				
1. Aspartic acid	6.4(0.18)	12.3(0.21)	17.0(0.21)	20.5(0.19)
2. Glutamic acid	11.1(0.32)	18.4(0.30)	23.5(0.31)	26.7(0.28)
3. Serine	13.5(0.39)	21.5(0.37)	26.1(0.34)	29.2(0.35)
Distance of separation between:				
(1) & (2)	4.7	6.1	6.5	6.2
(2) & (3)	2.4	3.1	2.6	2.5
II. Distance travelled by solvent front in each case 35.5 cm				
4. Threonine	19.4(0.55)	27.3(0.49)	31.3(0.49)	32.9(0.38)
5. Valine	28.0(0.79)	33.9(0.79)	35.5(0)	35.5(0)
Distance of separation between:				
(4) & (5)	8.6	6.6	4.2	2.6

TABLE II

DISTANCES TRAVELLED AND R_F VALUES FOUND DURING MULTIPLE DEVELOPMENT IN STRIP CHROMATOGRAPHY WITH BUTANOL-ACETIC ACID-WATER (4:1:1) AS THE DEVELOPING SOLVENT.
(d_1, d_2, d_3, d_4 are distances travelled in cm during first, second, third and fourth developments; R_F values are recorded in parentheses.)

Distance travelled by the solvent front in each case 42 cm

	d_1	d_2	d_3	d_4
1. Glycine & serine	6.4(0.15)	10.65(0.11)	13.85(0.10)	16.65(0.09)
2. Alanine	10.7(0.25)	17.15(0.20)	21.3(0.16)	24.2(0.13)
3. Proline	—	18.85(0.26)	23.2(0.18)	25.8(0.13)
Distance of separation between:				
(1) & (2)	4.3	6.5	7.45	7.55
(2) & (3)	—	1.7	1.9	1.6

Circular chromatography

The apparatus used in circular chromatography was as described previously[5]. Whatman's No. 1 filter circles 28 cm in diameter were used. Since the spraying of a circular chromatogram with the indicator after each development usually makes further development impossible and development of several chromatograms for determining R_F values at each stage of development becomes a quite laborious and tedious process, a simplified procedure was followed. After development and drying of a chromatogram, a thin section of it (as shown in Fig. 1) is cut out from the periphery

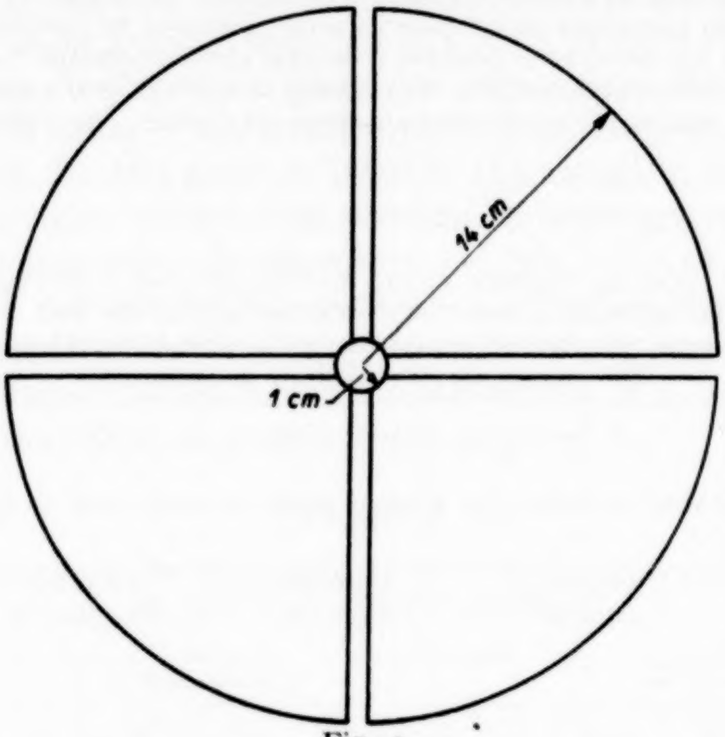

Fig. 1

TABLE III

DISTANCES TRAVELLED AND R_F VALUES FOUND DURING MULTIPLE DEVELOPMENT IN CIRCULAR CHROMATOGRAPHY WITH WATER-SATURATED PHENOL AS THE DEVELOPING SOLVENT.
(d_1, d_2, d_3, d_4 are distances travelled in cm during first, second, third and fourth developments; R_F values are recorded in parentheses.)

	d_1	d_2	d_3	d_4
I. Distance travelled by solvent front in each case 10.2 cm				
1. Glycine & serine	4.9(0.48)	6.2(0.24)	7.05(0.21)	7.7(0.20)
2. Alanine	6.45(0.63)	7.9(0.38)	8.55(0.28)	9.05(0.30)
Distance of separation between:				
(1) & (2)	1.55	1.7	1.5	1.35
II. Distance travelled by solvent front in each case 11.1 cm				
3. Aspartic acid	3.3(0.29)	4.6(0.16)	5.65(0.16)	6.25(0.10)
4. Glumatic acid	4.3(0.38)	5.8(0.22)	6.80(0.19)	7.25(0.10)
5. Threonine	6.2(0.56)	7.8(0.32)	8.8(0.30)	9.1(0.13)
6. Valine	8.2(0.74)	9.2(0.48)	10.3(0.46)	10.4(0.12)
Distance of separation between:				
(3) & (4)	1.0	1.2	1.15	1.0
(4) & (5)	1.9	2.0	2.0	1.85
(5) & (6)	2.0	1.4	1.5	1.3

up to the orbit of a small circle drawn around the centre. The strip so obtained is sprayed with a suitable indicating solution. The cut ends of the chromatogram are joined by threads so as to give it a complete circular form and the chromatogram is redeveloped. When the solvent front coincides with the front (marked with a pencil) travelled in the previous development, the chromatogram is taken out, dried and this time a second section, diametrical to the previous section is cut out and sprayed as before. Again the cut ends are joined with threads and the chromatogram is redeveloped. After the third and fourth developments sections at right angles to the first two sections are cut out and thus the distances travelled by the chromatographed substances during the successive stages of development can be easily followed. This avoids extra labour and further directly records the positions in successive developments with reference to positions in previous developments, which would not have been possible if several chromatograms had been developed for the purpose. It has also been observed that the cutting of sections in the manner described above does not affect the R_F values of the chromatographed substances. The results are given in Tables III and IV.

TABLE IV

DISTANCES TRAVELLED AND R_F VALUES FOUND DURING MULTIPLE DEVELOPMENT IN CIRCULAR CHROMATOGRAPHY WITH BUTANOL-ACETIC ACID-WATER (4:1:1) AS THE DEVELOPING SOLVENT. (d_1, d_2, d_3, d_4 are distances travelled in cm during first, second, third and fourth developments; R_F values are recorded in parentheses).

	d_1	d_2	d_3	d_4
I. Distance travelled by solvent front in each case 10.55 cm				
1. Glycine & serine	3.65(0.34)	4.9(0.18)	5.8(0.15)	6.35(0.11)
2. Alanine	4.9(0.46)	6.4(0.26)	7.25(0.20)	7.9(0.19)
Distance of separation between:				
(1) & (2)	1.25	1.5	1.45	1.55
II. Distance travelled by solvent front in each case 11.5 cm				
3. Aspartic acid & glumatic acid	3.95(0.34)	5.25(0.17)	6.15(0.14)	6.85(0.13)
4. Threonine	4.6(0.40)	6.25(0.24)	7.15(0.17)	7.85(0.16)
5. Valine	6.9(0.60)	8.7(0.39)	9.55(0.33)	10.0(0.23)
Distance of separation between:				
(3) & (4)	0.65	1.00	1.00	1.00
(4) & (5)	2.30	2.45	2.40	2.15

DISCUSSION

It is clear from Tables I and II that the generalizations arrived at from the theoretical considerations hold good, fairly well, in strip chromatography whatever the number of developments. Since, however, the R_F values depend upon a number of factors of which the distance of the starting point from the source of the developing solvent[6,7] becomes important in multiple development, the agreement between the calculated and observed values of the distances of separation may not be as close as desired. Thus, the R_F values obtained in multiple development (Tables I and II) are probably lowered due to this factor.

It is evident from Tables III and IV that the generalizations made in the case of strip chromatography hold fairly well for circular chromatography. For instance, the distance of separation between glycine, serine and alanine increases after the first development and actually the sum of the R_F values during the first development is less than unity (Table IV). With the same amino acids, however, but with a different developing solvent *viz.*, phenol-water instead of butanol-acetic acid-water, the distance of separation is found to increase during second development (Table III) though a decrease is expected from the generalizations made earlier. The deviations from the generalizations are due, probably to a great extent to the variation of R_F values in successive developments. That this variation in R_F value is related to an increase in the distance of the starting point from the source of the developing solvent is clear from the data given in Table V. The change in R_F values in circular chromatography is more marked than in strip chromatography. Though the R_F values decrease in successive developments and the value of the expression $\{1 - (R_{F_1} + R_{F_2})\}$ increase, better separation is expected in subsequent developments but this is not found to be so experimentally in a number of cases. It should, however, be remembered that the rate of travel of solutes on a circular chromatogram is always greater than that on a strip chromatogram[8].

TABLE V

EFFECT OF THE DISTANCE BETWEEN THE STARTING POINT AND THE SOLVENT SOURCE ON R_F VALUES IN CIRCULAR CHROMATOGRAPHY

Solvent	*Phenol-water*					*Butanol-acetic acid-water*				
Distance in cm	1	3	5	7	9	1	3	5	7	9
Aspartic acid	0.24	0.15	0.12	0.10	0.13	0.31	0.22	0.20	0.17	0.17
Serine	0.42	0.36	0.28	0.23	0.21	0.30	0.24	0.20	0.18	0.16
Threonine	0.52	0.48	0.41	0.38	0.30	0.36	0.31	0.26	0.21	0.19
Alanine	0.59	0.54	0.47	0.43	0.35	0.42	0.36	0.31	0.26	0.20
Valine	0.75	0.72	0.69	0.63	0.60	0.55	0.50	0.45	0.38	0.34

It is further observed from the Tables II and III that glycine and serine cannot be separated by any of the two solvents even after four successive developments. Further development will be of no help as the distance travelled by the spot composed of the two has already crossed half the distance travelled by the solvent front.

Multiple development technique is more extensively applied in circular chromatography since in this case multiple development is found to effect better and neater separations. Theoretical reasoning aside, it is evident that in circular chromatography the constituents separate out either in the form of arcs or rings, and that with increasing distance of travel these become narrower in width due to advancement on a wider front. Therefore it is not surprising that multiple development will aid separation between two overlapping constituents by narrowing down the widths of both.

Thus, the generalizations arrived at for multiple development, when applied to circular chromatography, become of immense help in deciding whether multiple development is necessary in certain separations. It can also be decided earlier how many successive developments are to be carried out for the purpose.

References p. 456.

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SUMMARY

Some conditions have been derived from which it appears that in multiple development the distance of separation between two spots on strip and circular chromatograms should increase or decrease according as the sum of their R_F values is less than or greater than unity. When the sum equals unity, there should be no change.

Experimental evidence has been put forward in support of the above generalizations. The deviations of the theoretical from the experimental values are largely due to the changes in R_F values in successive developments.

RÉSUMÉ

Des conditions ont été établies, à partir desquelles il semble que lors d'un développement multiple, la distance de séparation entre deux taches obtenues sur des chromatogrammes (sur bande ou circulaires) devrait augmenter ou diminuer, suivant si la somme des valeurs de R_F est plus faible ou plus grande que l'unité. Lorsque cette somme est égale à l'unité, il n'y aurait pas de déplacement. Des expériences ont prouvé les hypothèses ci-dessus. Les différences observées entre les valeurs théoriques et expérimentales sont dues en grande partie aux variations des valeurs de R_F lors des développements successifs.

ZUSAMMENFASSUNG

Es wurde gezeigt, dass bei mehrfacher Entwicklung der Abstand zwischen zwei Flecken auf Banden- oder Zirkularchromatogrammen theoretisch zu- oder abnehmen sollte, je nachdem die Summe der R_F-Werte kleiner oder grösser als 1 ist. Ist diese Summe gleich 1, so sollte keine Verschiebung stattfinden.

Diese allgemeinen Aussagen werden durch Versuchsergebnisse gestützt. Die Abweichungen zwischen den theoretischen und experimentellen Werten sind grösstenteils auf die Änderungen der R_F-Werte bei mehrfacher Entwicklung zurückzuführen.

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MICRO-HETEROMETRIC DETERMINATION OF TRACES OF ZINC IN SOLUTIONS AND ALLOYS WITH SODIUM DIETHYLDITHIOCARBAMATE

by

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INTRODUCTION

The heterometric determination of zinc with sodium diethyldithiocarbamate (= CBM) is very sensitive and compares well with other sensitive and selective reactions studied previously. It is almost as sensitive and precise as the determination of copper with CBM[1] and as the determination of cobalt with α-nitroso-β-naphtol[2]. Unfortunately the pH-dependence of the reaction and the heterometric sensitivity of zinc-carbamate towards supplements and complexing agents makes the direct heterometric determination of zinc possible only in the presence of excesses of a few foreign metals. They are: Ca^{+2}, Sr^{+2}, Ba^{+2}, Mg^{+2}, Al^{+3}, Cr^{+3} and Mn^{+2}. Under appropriate conditions, these metals, even when present in solution in large amounts do not influence the maximum density values. Therefore, the same amount of zinc was used in all cases for the analysis, whether a foreign metal was present or not. The analysed solutions contained 0.2-0.4 mg of zinc in 20 ml aqueous solution (concentration: $1.5\text{-}3 \cdot 10^{-4}M$). This made up 0.03-0.2% of the total metal content.

In some cases the heterometric determination could be made more sensitive by using a blue filter (see below) and the concentration of zinc was then as low as $1 \cdot 10^{-4}\text{-}5 \cdot 10^{-5}M$.

Most of the titrations lasted about 10 minutes and the heterometric determination of zinc with carbamate can therefore be used very successfully in all the abovementioned cases.

EXPERIMENTAL

Chemicals and solutions

The reagents used were all either AnalaR or chemically pure. The sodium diethyldithiocarbamate was an Eastman Chemicals reagent. A 0.06M stock solution was prepared. The solution was kept in darkness and was stable for months. The solutions used were standardized against copper sulphate. The dilute solutions were freshly prepared every 2-3 days.

Apparatus and working conditions

The same apparatus and the same working conditions were employed as in previous heterometric investigations[3]. The fundamentals of heterometry are presented in a separate paper[4]. The temperature of the reaction vessel (4.6 cm diameter) was thermostatically controlled during the titration. All titrations were carried out at 20°C.

TABL

Composition: 3 ml aM $ZnSO_4$ + A ml supplements + (17-A) ml H_2O + x ml 0.0027M sodium die

Exp. No.	*Molarity of $ZnSO_4$(a)*	*Supplements*
1	0.002	17 ml H_2O
2	0.00133	17 ,, ,,
3	0.001	17 ,, ,,
4	0.00133	1 ,, M CH_3COOH
5	0.001	1 ,, 0.1M ,,
6	0.00133	1 ,, 0.1M ,,
7	0.00133	4 ,, M ,,
8	0.002	1 ,, 0.1M HNO_3
9	0.002	1 ,, M CH_3COOH
10	0.002	1 ,, M ,, + 2 ml M NH_4NO_3
11	0.00133	1 ,, M CH_3COONa
12	0.002	4 ,, ,, ,,
13	0.002	2 ,, ,, NH_3
14	0.002	2 ,, ,, ,, + 2 ml M NH_4NO_3
15	0.002	3 ,, ,, K_2-tartrate
16	0.00133	3 ,, ,, ,,
17	0.002	2 ,, ,, Na_3-citrate
18	0.00133	10 ,, 0.1M $Na_4P_2O_7$
19	0.002	3 ,, M K_2-tartrate + 1 ml M CH_3COOH
20	0.002	2 ,, ,, Na_3-citrate + 1 ,, ,, ,,
21	0.002	1 ,, ,, ,, + 2 ,, ,, NH_3 + 4 ml M NH_4NO_3
22	0.002	3 ,, ,, ,, + 2 ,, ,, ,, + 2 ,, ,, ,,
23	0.00133	3 ,, ,, K_2-tartrate + 2 ml M NH_3
24	0.002	3 ,, ,, ,, + 2 ,, ,, ,, + 2 ml M NH_4NO_3
25	0.00133	3 ,, ,, ,, + 2 ,, ,, ,, + 2 ,, ,, ,,
26	0.002	2 ,, ,, CH_3COONa + 1 ,, ,, KCN
27	0.002	2 ,, ,, NH_3 + 2 ml M NH_4NO_3 + 1 ml M KCN
28	0.00133	2 ,, ,, Na-salicylate

* = after the maximum point, fluctuation; ** = horizontal maximum density line;

The end-point of the titration was obtained in all cases from enlarged titration curves in the following way: a line was drawn through the density points of the last part (= quarter) of the titration curve. Another line was drawn through the maximum density points. The intersection of both lines gave the end-point of the titration (= x).

Generally, no filter was used as the salt solutions were colourless. In special cases a blue Corning filter was used in order to increase the sensitivity of the reaction (see below).

RESULTS AND DISCUSSION

Tables I and II and Fig. 1 (the same numeration is used in both cases) present a selection of experiments, their composition and the results obtained. Table I shows the composition and the results of experiments which were carried out in the absence of foreign metals, whilst Table II contains results which were obtained in the presence of large excesses of foreign metals. In all experiments shown in Table II, a horizontal maximum density line was obtained after the first maximum density point. Only in exp. 52 was no smooth curve obtained. Exp. 66 gave a pink and exp. 67 a red precipitate.

Experiments in the absence of foreign metals

Analysing the results of Table I, the following may be deduced: in neutral solution, no proportionality seemed to exist between the maximum density values obtained and the amount of zinc present in the analysed solutions (exps. 1-3).

Generally, the presence of *acetic acid* hardly influenced the results (exps. 4-6).

iocarbamate (CBM). T = 20°C. Content: 0.196-0.392 mg zinc ($1.5\text{-}3 \cdot 10^{-4} M$)

Theoretical point at ml	*ml CBM(x)*	*Max. density value*	*Initial precip. at ml*	*Titration time (min)*	*Error (%)*
4.5	4.50	0.76	0.2	10	0.0
3.0	3.00	0.65	0.2	9	0.0
2.25	2.24	0.52	0.2	7	−0.4
3.0	3.0	0.43*	0.2	18	0.0
2.25	2.30	0.41*	0.2	15	+2.2
3.0	3.0	0.51*	0.2	17	0.0
3.0	3.0	0.30*	0.8	15	0.0
4.5	4.46	0.34*	0.2	20	1.0
4.5	4.50	0.65**	0.2	8	0.0
4.5	4.50	0.58**	0.2	9	0.0
3.0	3.00	0.58**	0.2	14	0.0
4.5	4.50	0.75**	0.2	15	0.0
		0.0	∞		
4.5	4.50	0.63	0.2	13	0.0
4.5	4.50	0.65**	0.2	14	0.0
3.0	3.00	0.42**	0.2	11	0.0
		∼0.3***	2.4		
		0.0	∞		
4.5	4.6	0.62**	0.2	15	+2.2
4.5		0.32*	1.4	30	
4.5	4.50	0.48**	1.0	15	0.0
4.5	4.50	0.37**	1.4	18	0.0
		0.0	∞		
4.5	4.50	0.60**	0.2	15	0.0
3.0	2.96	0.45**	0.2	15	−1.3
		0.0	∞		
		0.0	∞		
3.0	2.96	0.60**	0.2	8	−1.3

= no clear end-point.

In the presence of large amounts of acetic acid the solubility of zinc-carbamate was noticeably increased: the initial precipitation occurred later and the maximum density values obtained was low (exp. 7). In addition, the maximum density values after the end-point, fluctuated. When the amount of zinc was somewhat larger (exp. 9) a stable, horizontal maximum density line was obtained.

In the presence of dilute *nitric acid* (exp. 8) the maximum density value was low and showed fluctuations (compare exps. 1 and 8).

In the presence of *sodium acetate* (exps. 11 and 12) a stable, horizontal maximum density line was obtained, thus making it possible to fix, with certainty, the location of the end-point. In addition, the maximum values were higher with the larger amounts of acetate.

In pure *ammonia* (exp. 13) no precipitation of zinc-carbamate occurred.

In solutions which contained a mixture of *ammonia-ammonium nitrate* (exp. 14) the titration went smoothly till the first maximum density point was reached, then the density dropped slowly with further addition of titrant.

In the presence of a neutral solution, which contained large excesses of *potassium tartrate*, the maximum density values obtained were normal. A horizontal maximum density line was obtained after the theoretical end-point. A similar result was obtained when acetic acid was added (exp. 19).

TABLE

Composition: 3 ml $0.002M$ $ZnSO_4$ + A ml supplements + (17-A) ml H_2O + x ml $0.0027M$ CBM.

Exp. no.	Content Supplements	 Foreign metal (mg)
29	2 ml M $Ca(NO_3)_2$	80.16
30	2 ,, ,, ,, + 2 ml $0.1M$ CH_3COOH	
31	10 ,, ,, ,, + 2 ,, ,, ,,	400.8
32	5 ,, ,, ,, + 2 ,, M CH_3COONa	
33	2 ,, ,, $SrCl_2$	175.26
34	2 ,, ,, ,, + 2 ,, $0.1M$ CH_3COOH	
35	10 ,, ,, ,, + 2 ,, ,, ,,	876.3
36	10 ,, ,, ,, + 2 ,, M CH_3COONa	
37	2 ,, ,, $BaCl_2$	274.74
38	2 ,, ,, ,, + 2 ,, $0.1M$ CH_3COOH	
39	10 ,, ,, ,, + 2 ,, ,, ,,	1373.7
40	5 ,, ,, ,, + 2 ,, M CH_3COONa	
41	2 ,, ,, $MgCl_2$	48.64
42	10 ,, ,, ,,	243.2
43	2 ,, ,, ,, + 1 ,, ,, CH_3COOH	48.64
44	10 ,, ,, ,, + 2 ,, $0.1M$,,	243.2
45	10 ,, ,, ,, + 2 ,, M CH_3COONa	243.2
46	10 ,, ,, ,, + 2 ,, ,, NH_3 + 2 ml M NH_4NO_3	243.2
47	2 ,, ,, $AlCl_3$	53.94
48	2 ,, ,, ,, + 2 ,, $0.1M$ CH_3COOH	53.94
49	5 ,, ,, ,, + 2 ,, ,, ,,	134.85
50	10 ,, ,, ,, + 2 ,, ,, ,,	269.7
51*	2 ,, ,, ,, + 4 ,, M CH_3COONa	53.94
52	2 ,, ,, $Al(NO_3)_3$ + 1 ,, ,, ,, + 3 ml M K_2-tartrate	53.94
53	2 ,, ,, $AlCl_3$ + 2 ,, ,, NH_3 + 2 ml M NH_4NO_3 + 4 ml M K_2-tartrate	
54	0.5 ,, ,, $Cr(NO_3)_3$ + 2 ,, $0.1M$ CH_3COOH	26.0
55	1 ,, ,, ,, + 2 ,, ,, ,,	52.01
56	1 ,, ,, ,, + 2 ,, M CH_3COONa	52.01
57	2 ,, ,, ,, + 4 ,, ,, ,,	104.02
58	5 ml M $Cr(NO_3)_3$ + 5 ml $2M$ CH_3COONa	260.05
59	2 ,, ,, NH_3 + 2 ml M NH_4NO_3 + 3 ml M K_2-tartrate + 1 ml M $FeCl_3$	
60	2 ,, ,, ,, + 2 ,, ,, ,, + 1 ,, ,, Na_3-citrate + 0.5 ,, ,, ,,	
61	4 ,, ,, CH_3COONa + 1 ml M $FeCl_3$	
62	2 ,, ,, NH_3 + 2 ml M K_2-tartrate + 2 ml $0.1M$ $FeCl_3$	
63	2 ,, $0.1M$ CH_3COOH + 2 ml M K_2-tartrate + 1 ml M $MnCl_2$	54.93
64	2 ,, ,, ,, + 4 ,, ,, ,, + 2 ,, ,, ,,	109.86
65	2 ,, ,, ,, + 5 ,, ,, ,, + 3 ,, ,, ,,	164.79
66	2 ,, ,, ,, + 10 ,, ,, ,, + 5 ,, ,, ,,	274.65
67	2 ,, M NH_3 + 2 ml M NH_4NO_3 + 4 ml M K_2-tartrate + 2 ml M $MnCl_2$	109.86

* 3 ml $0.00133M$ $ZnSO_4$

Tartrate solutions which contained, in addition, *ammonia-ammonium nitrate* (exps. 24 and 25) gave the same results as were obtained in the absence of the latter, (compare exps. 15 and 16 with experiments 24 and 25). In contrast to these no precipitation occurred when ammonia only was added to the tartrate solution (exp. 23).

On the basis of these experiments it may be concluded that *in the presence of excesses of potassium tartrate, whatever the pH, the heterometric determination of zinc remains unaffected.*

In contrast to this were the results obtained in the presence of excesses of *trisodium citrate.* In neutral solution (exp. 17), as the zinc is probably complexed by the citrate, precipitation occurred very late and no clear end-point was reached. In acetic acid

= 20°C. Content: 0.392 mg Zn

		Found			
Zinc (%)	*ml CBM (x)*	*Maximum density value*	*Initial precip. at ml*	*Titration time (min)*	*Error (%)*
0.5	4.50	0.64	0.2	11	0.0
	4.50	0.60	0.2	14	0.0
0.1	4.50	0.58	0.2	10	0.0
	4.50	0.65	0.2	9	0.0
0.2	4.50	0.64	0.2	10	0.0
	4.50	0.58	0.2	12	0.0
0.05	4.52	0.60	0.2	9	0.4
	4.47	0.65	0.2	8	0.6
0.14	4.5	0.65	0.2	9	0.0
	4.50	0.59	0.2	10	0.0
0.03	4.50	0.57	0.2	7	0.0
	4.50	0.71	0.2	8	0.0
0.8	4.50	0.66	0.2	11	0.0
0.16	4.50	0.64	0.2	13	0.0
0.8	4.50	0.50	0.2	11	0.0
0.16	4.50	0.45	0.2	15	0.0
0.16	4.50	0.76	0.2	8	0.0
0.16	4.50	0.69	0.2	11	0.0
0.7	4.50	0.55	0.2	14	0.0
0.7	4.45	0.51	0.2	14	—1.2
0.3	4.46	0.45	0.2	13	—0.9
0.14		∞0.40	0.2		
0.47	3.00	0.52	0.2	10	0.0
0.7	4.50	0.51	0.2	13	0.0
	4.50	0.34	0.2	10	0.0
1.5	4.45	0.49	0.2	16	—1.2
0.7	4.46	0.29	0.2	19	—0.9
0.7	4.46	0.68	0.2	10	—0.9
0.37	4.5	0.24	0.2	11	0.0
0.15	4.50	0.24	0.4	12	0.0
	∞	>0.70	0.2	10	
	∞	>0.93	0.2	15	
	∞	>0.45	0.2	10	
	∞	>1.00	0.2	14	
0.7	4.50	0.48	0.2	13	0.0
0.4	4.50	0.61	0.2	10	0.0
0.2	4.48	0.55	0.2	13	—0.4
	∞	>0.46	0.2	16	
	∞	>0.62	0.2	20	

solution (exp. 20) the initial precipitation also occurred late and no clear density line was obtained. In *ammonia-ammonium nitrate* solution (exps. 21 and 22), clear end-points were obtained but here too the initial precipitation occurred late and the maximum density values were low.

In the presence of excesses of *sodium pyrophosphate* no precipitation occurred at all.

No precipitation occurred in the presence of excesses of *potassium cyanide* either in acetate or in ammoniacal solution.

No precipitation occurred in solutions which contained *pure ammonia* (exps. 13 and 23). As in the case with tartrate, excesses of *sodium salicylate* (exp. 28) had no deteriorating effect on the precipitation of zinc carbamate.

Summarizing, it may be said, that zinc can be determined successfully either in acetic acid or in sodium acetate solutions. Amongst the complexing agents which could be used successfully in large excess, alkali tartrate took the first place. It could be used with the same success in acetic acid, acetate or ammoniacal solutions. But in the last case ammonium nitrate had to be added.

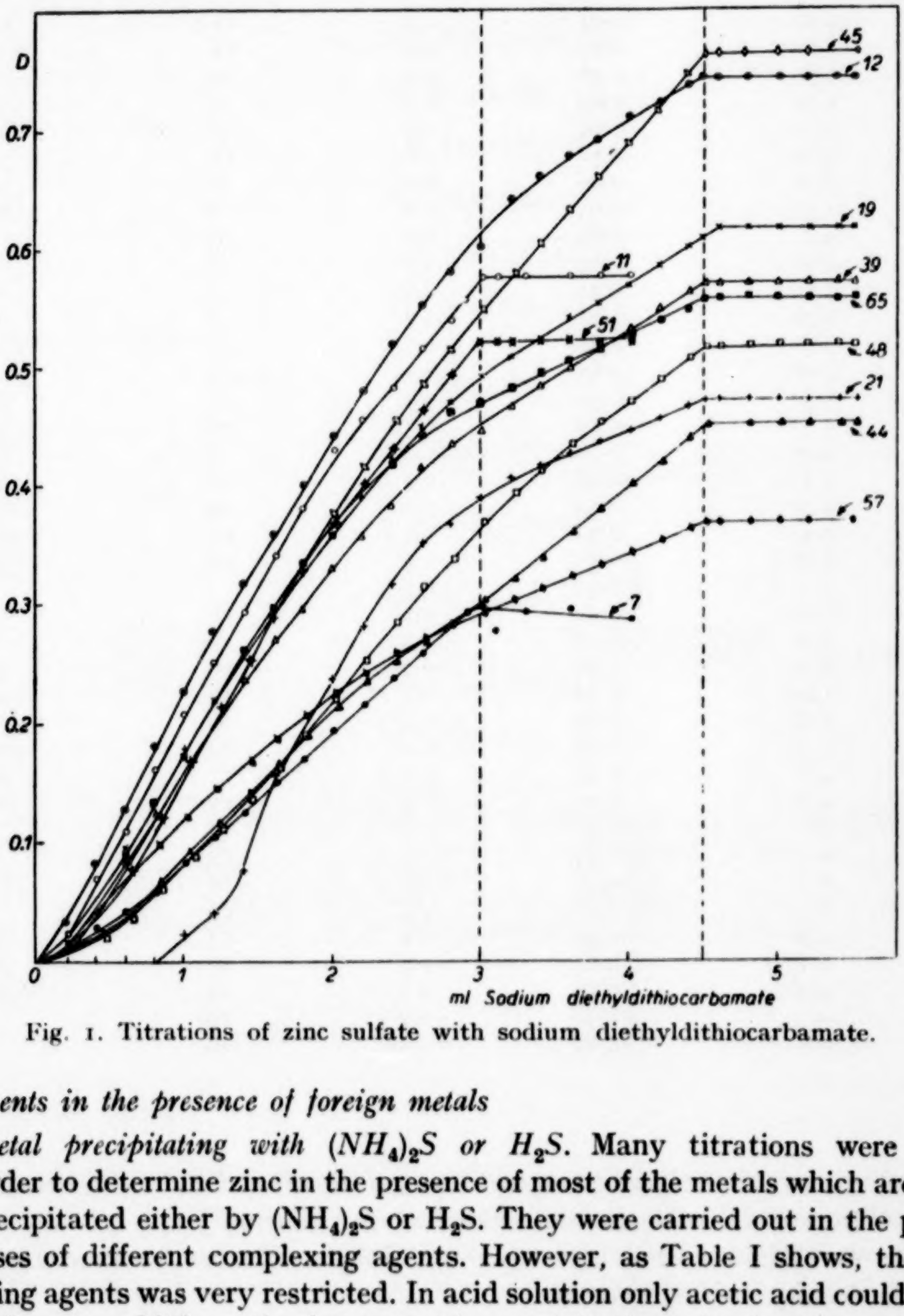

Fig. 1. Titrations of zinc sulfate with sodium diethyldithiocarbamate.

Experiments in the presence of foreign metals

a) *Metal precipitating with $(NH_4)_2S$ or H_2S.* Many titrations were carried out in order to determine zinc in the presence of most of the metals which are known to be precipitated either by $(NH_4)_2S$ or H_2S. They were carried out in the presence of excesses of different complexing agents. However, as Table I shows, the use of complexing agents was very restricted. In acid solution only acetic acid could be used successfully. In addition, the heterometric precipitation of minute quantities of zinc was very sensitive to the supplements used, and, in consequence, a greater amount of zinc was necessary in order to obtain safe results (compare exps. 4-6 with exp. 9).

As Table II shows, *direct* titrations of zinc in the presence of foreign metals could only be carried out successfully in the presence of excesses of Ca^{+2}, Sr^{+2}, Ba^{+2}, Al^{+3},

Cr^{+3} and Mn^{+2}. The results of Table II will therefore be discussed first and later on a brief account will be given of the results with the other metals. In almost all the above cases an acetic acid solution was used. With manganese good results were obtained only with solutions containing large excesses of potassium tartrate, in addition to the acetic acid used. Table II contains experiments in the presence of *sodium acetate* instead of dilute acetic acid (exps. 32, 36, 40, 42, 48 and 53). In all cases the maximum densities obtained were higher than in the presence of dilute acetic acid. In the presence of aluminium (exp. 51) the analysed zinc was able to be reduced to half the amount which was usually used because of the high density obtained. It may therefore be assumed that in all cases presented in the table, the acetic acid can be advantageously replaced by sodium acetate. This of course depends on the general composition of the analysed metal or alloy.

In no case did the use of potassium tartrate in acetate or ammonia solutions (exps. 52 and 53) present an advantage when compared with similar experiments carried out in the absence of tartrate. In the case of ferric iron and manganese no end-point was obtained when ammoniacal citrate or tartrate solutions were used. Negative results were also obtained in the presence of iron solutions which contained large excesses of sodium acetate (exp. 61). This is surprising as generally such solutions help to mask the iron.

As to the percentage of zinc in the analysed solutions, in the case of barium it was as low as 0.03%, but generally it made up 0.1-0.2% of the total metal content. The titration time was in many cases approximately 10 minutes; in a few cases it was somewhat longer. Of course this also depends on the experience gained with the particular compound analysed. The greater the experience possessed, the shorter the titration time necessary.

In almost all cases the end-point obtained from the curves coincided with the calculated end-point and the error was nearly zero.

b) *Other metals*. Many experiments were carried out in the presence of excesses of other metals such as nickel, cobalt, cadmium, lead etc. They were carried out in 1) acetic acid, 2) sodium acetate, 3) NH_3/NH_4NO_3 solutions which contained excesses of Na_3-citrate or K_2-tartrate.

These experiments were unsuccessful and the results may be summarized briefly.

Nickel nitrate (2 ml 0.1 M). In all cases the densities increased continuously beyond the calculated end-point.

Cobalt nitrate (2 ml 0.1 M). The densities were low and they fluctuated. No clear end-point was reached.

Cadmium nitrate (0.2-0.5 ml M). A white precipitate was obtained. In almost all cases the density rose continuously beyond the calculated end-point. Only in the case of potassium tartrate, which contained an excess of NH_3/NH_4NO_3 was a maximum density point reached at the calculated end-point. Immediately after the attainment of this point the precipitate coagulated. Unfortunately the result was not consistently reproducible. In another experiment with an excess of potassium tartrate to which acetic acid had been added, the titration could also be carried out till the end-point but then the precipitate coagulated.

Lead nitrate (2 ml 0.1 M). In both cases with ammoniacal citrate or tartrate solutions the titrations went smoothly and a white precipitate was formed but the density rose continuously beyond the calculated end-point.

Titrations with filtered light

Many experiments were carried out by the first author with co-workers in order to increase the sensitivity of the heterometric titrations by using a red or blue filter and titrating uncoloured solutions. Corning filters were used which are supplied with the Fisher Electrophotometer.

Parallel experiments carried out by us with the above filters gave the following results: when a red filter was used instead of the regular bulb light, the maximum density value was somewhat lower. When a blue filter was used, the maximum density value was about twice as high as when no filter was used, and in some cases the molarity of the titrated zinc sulphate solution could be as low as $\sim 0.5 \cdot 10^{-5} M$. But as can be seen from Table I, the use of solutions of low molarity causes fluctuations and makes the determination unreliable. These fluctuations disappear when a higher amount of zinc is used.

Method

20 ml aqueous solution containing 0.2-0.4 mg zinc and acidified with acetic acid (2 ml $0.1M$) is titrated heterometrically with an aqueous solution of $\sim 0.003M$ sodium diethyldithiocarbamate. The solution may contain 99.7-99.9% of calcium, strontium, barium, magnesium, aluminium, chromium(III) or manganese(II). Titration time 7-15 minutes. Error: generally 0-1%.

Remarks:

1) When excesses of manganese are present, the acidified solution must contain alkali tartrate in a molar amount which is at least about twice as high as the estimated amount of manganese.

2) The reaction is more sensitive and higher densities are obtained if 2 ml M sodium acetate are added to the analysed solution (either to the neutral or to the acidified solution).

SUMMARY

0.2-0.4 mg zinc in 20 ml aqueous solution can be determined heterometrically with sodium diethyldithiocarbamate. The solution may contain up to $\sim$99.8% of Ca, Sr, Ba, Mg, Al, Cr(III) or Mn(II). The titrations take about 10 minutes and the error is 0-1%.

RÉSUMÉ

0.2-0.4 mg de zinc, peuvent être dosés par la méthode hétérométrique, dans une solution aqueuse, au moyen du diéthyldithiocarbamate de sodium. La solution peut renfermer jusqu'à $\sim$99.8% de Ca, Sr, Ba, Mg, Al, Cr(III) ou Mn(II). Le titrage exige environ 10 minutes, et l'erreur est de 0-1%.

ZUSAMMENFASSUNG

0.2-0.4 mg Zink können in 20 ml wässriger Lösung mit Hilfe von Natriumdiäthyldithiokarbamat bestimmt werden. Die Lösung kann bis zu $\sim$99.8% an Ca, Sr, Ba, Mg, Al, Cr(III) oder Mn(II) enthalten. Titrationsdauer etwa 10 Minuten. Fehler: 0-1%.

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COULOMETRIC TITRATION OF IRON, CERIUM AND VANADIUM WITH TITANOUS ION

by

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ARTHUR AND DONAHUE[1] originated the use of electrogenerated titanous ion for coulometric titrations, and applied the technique to the determination of ferric ion. They employed a gold generator cathode, a supporting electrolyte composed of $0.4M$ titanic chloride in $0.7M$ hydrochloric acid, and titrated 50 to 110 mg quantities of ferric ion with an average accuracy of about ±0.3% Our experience indicates that the actual current efficiency for titanous ion generation — as distinct from net titration efficiency — in a solution of hydrochloric acid as dilute as $0.7M$ is much smaller than 100%, and the high net titration efficiency observed by ARTHUR AND DONAHUE must have resulted from a major fraction of the ferric ion being directly electroreduced at the gold cathode, so that the error from less than 100% current efficiency for generation of titanous ion was greatly minimized.

The difficulties observed by PARSONS AND SEAMAN[7] when they attempted the titration of various dyestuffs by the technique of ARTHUR AND DONAHUE very probably stemmed from the slight tendency for such compounds to undergo direct electroreduction, so that the titration has to proceed almost entirely via generation of titanous ion. In such cases, less than 100% current efficiency for titanous ion generation causes an equal error in the net titration efficiency.

PARSONS AND SEAMAN demonstrated that the use of the high hydrogen overvoltage mercury cathode permits the generation of titanous ion (from $0.4M$ titanic chloride and $0.7M$ hydrochloric acid) with 100% current efficiency even up to current densities as large as 400 milliamp/cm^2. LINGANE AND IWAMOTO[3] also employed a mercury cathode for the coulometric titration of +6 uranium with electrogenerated titanous ion in an acidic citrate medium. The titration error is so small (less than ± 0.05%) that the technique can be employed for precision assays of uranium compounds.

MALMSTADT AND ROBERTS[6] discovered that a titration efficiency of 100% can be obtained when titanous ion is generated at a titanium or platinum cathode provided the hydrochloric acid concentration is $7M$ or greater. Since a platinum generator cathode is much more convenient to use than a mercury cathode, this discovery paved the way for extensive practical exploitation of coulometric titrations with titanous ion.

LINGANE AND KENNEDY[4] showed that the beneficial effect of a very large concentration of hydrochloric acid results from the fact that the overpotential for reduction of titanic chloride is so greatly decreased in strong hydrochloric acid that it more than compensates for the easier reduction of hydrogen ion. Consequently the difference between the reduction potentials of the titanic chloride complex and hydrogen ion — which is the prime factor governing the current efficiency — is markedly increased the higher the hydrochloric acid concentration.

The polarographic measurements of LINGANE AND KENNEDY demonstrated that +4 titanium is reduced more reversibly in sulfuric or phosphoric acids than in the same concentration of hydrochloric acid, so that a sulfuric acid medium (4 to 10M) should be more advantageous than a hydrochloric acid solution for coulometric titrations with titanous ion using a platinum generator cathode. The present study confirmed this prediction.

A sulfuric acid medium is more convenient to work with than moderately concentrated hydrochloric acid, and it extends the scope of coulometric titration with titanous ion to the determination of oxidants (like ceric, dichromate, or permanganate ions) which would be reduced by chloride ion.

For polarographic determination of either +4 or +3 titanium, phosphoric acid media (2M or greater) are superior in most respects to any other supporting electrolyte. However, phosphoric acid solutions are impractical for coulometric titrations with titanous ion, because the maximal concentration of +4 titanium which can be kept in stable solution is only of the order of 0.01M, a concentration adequate for polarographic titanium determinations but too small to serve as a supporting electrolyte in coulometric titrations.

Current efficiency for electrogeneration of +3 titanium at a platinum cathode

Current efficiencies for the reduction of +4 titanium in hydrochloric and sulfuric acid media were estimated from current-cathode potential curves with and without +4 titanium present. The same cell and platinum cathode (area 14.9 cm^2) used for the coulometric titrations was employed. The potential of the cathode was measured against an external saturated calomel electrode, and with the sulfuric

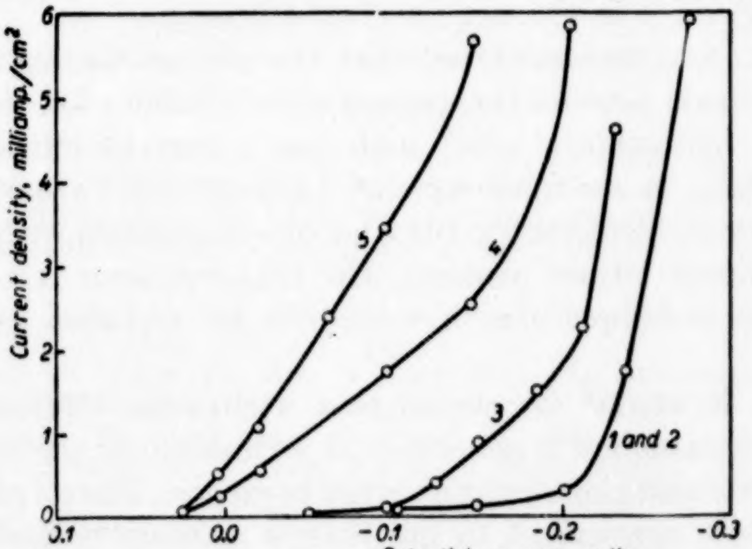

Fig. 1. Current-potential curves of +4 titanium reduction in hydrochloric acid. (1) 4M hydrochloric acid alone, (2) 0.3M titanium in 4M hydrochloric acid, (3) 8M hydrochloric acid alone, (4) 0.3M titanium in 8M hydrochloric acid, and (5) 0.6M titanium in 8M hydrochloric acid.

acid solutions a sulfuric acid salt bridge was used to avoid contamination of the test solution with chloride ion. The solutions were stirred efficiently with a magnetic stirrer.

Typical current-cathode potential curves in hydrochloric and sulfuric acid media are shown in Figures 1 and 2. The current efficiency for generation of +3 titanium as a function of the total current density and the concentration of +4 titanium in various concentrations of hydrochloric and sulfuric acids is shown more explicitly in Fig. 3. These curves were derived from the current-potential curves on the assumption that the current efficiency for generation of titanous ion is given by $(i\text{-}i_H)/i$, where i is the total current at a given current density (or given cathode potential) and i_H is the corresponding current at the same cathode potential observed with the acid solution alone.

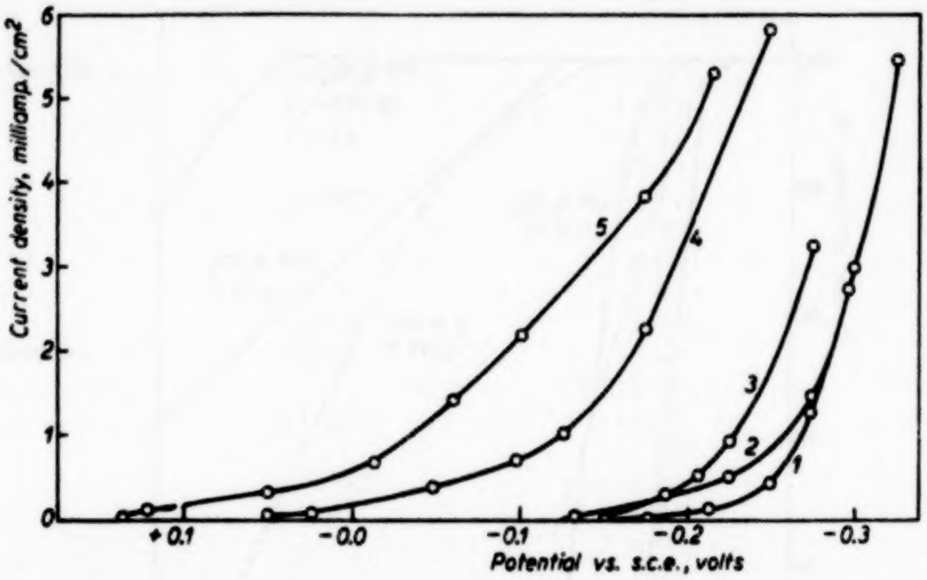

Fig. 2. Current-potential curves of +4 titanium reduction in sulfuric acid. (1) 2*M* sulfuric acid alone, (2) 0.3*M* titanium in 2*M* sulfuric acid, (3) 7*M* sulfuric acid alone, (4) 0.3*M* titanium in 7*M* sulfuric acid, and (5) 0.6 *M* titanium in 7*M* sulfuric acid.

It should be emphasized that the curves have quantitative significance only for the particular conditions of stirring, cell geometry, and concentration of +4 titanium, used; the limiting current density above which the current efficiency falls below 100% is greater the more efficient the stirring (up to a limit) and the greater the concentration of +4 titanium.

The limiting current density in hot solutions is somewhat smaller than at room temperature, with other conditions the same, because the reduction potential of hydrogen ion decreases more than that of +4 titanium with an increase of temperature.

The current efficiencies predicted by the current-potential curves were verified by directly determining the amount of +3 titanium produced under a particular set of conditions as follows. The +4 titanium solution, from which air had been removed with nitrogen, was electrolyzed with a known current for a measured time. An amount of ferric iron about 5% in excess of the amount of +3 titanium formed was then added, and the titration was continued to an amperometric end-point as described in a following section. The results obtained agreed well with the predictions of Fig. 3. For example, with a generating current density of 0.96 milliamp/cm², and 0.3M titanic chloride, the directly determined current efficiencies with 6 and 8M hydrochloric acid were respectively 80 and 99.8%, compared to 82 and 100% predicted from Fig. 3. With 4M sulfuric acid and 0.5M titanic sulfate, at a current density of 0.96 milllamp/cm², the directly determined current efficiency was 99.2% compared to 94% predicted from Fig. 3.

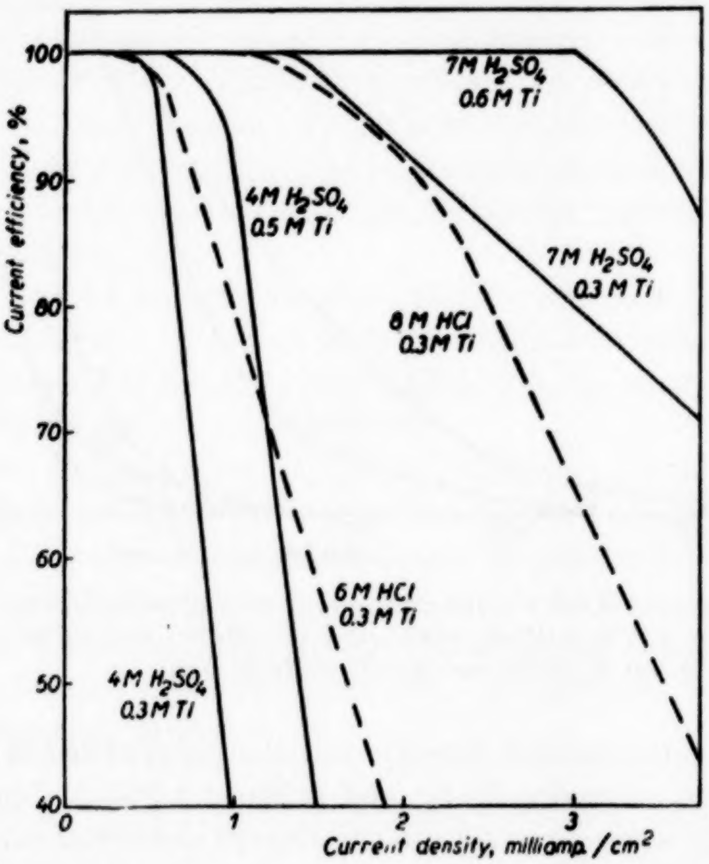

Fig. 3. Effect of solution composition and current density on current efficiency for generation of +3 titanium at a platinum cathode.

Coulometric titration of iron, cerium, and vanadium

Ferric iron, +4 cerium, and +5 vanadium were titrated in a supporting electrolyte composed of 6 to 8M sulfuric acid and 0.3 to 0.6 M titanic sulfate, using both potentiometric and amperometric end-point detection.

The titration cell consisted of a 125 ml tall form, lipless beaker closed by a rubber stopper. The generator cathode was of platinum foil with an area of 14.9 cm². The auxiliary anode was a cadmium rod in 1M sulfuric acid, contained in a glass tube, whose bottom was closed by a sintered glass disk, and which was immersed in the test solution. A platinum auxiliary anode was not used for fear that the oxygen produced at it would diffuse into the test solution. Air was removed from the test solution with nitrogen, and a magnetic stirrer provided efficient stirring.

Potentiometric end-point detection, with a platinum indicator electrode and saturated calomel reference electrode, followed the usual familiar practice[2].

The amperometric detection system comprised two identical platinum electrodes (area 1 cm² each) across which a constant small voltage was maintained. The indicator current was observed with a microammeter.

Iron

The typical results in Table I demonstrate that quantities of ferric iron from about 2 to 23 mg in 100 ml can be titrated with an average error of somewhat less than +0.3% by either end-point detection technique.

TABLE I

COULOMETRIC TITRATION OF FERRIC IRON

The supporting electrolyte (volume *ca.* 100 ml) consisted of 6 to 8*M* sulfuric acid and 0.3 to 0.6*M* titanic sulfate. Generating currents from 10 to 25 milliamp (current density 0.7 to 1.7 milliamp/cm²) were used, to provide titration times of 200 to 1000 seconds.

End-point detection	*Ferric iron, mg*		*Error %*
	Taken	*Found*	
Potentiometric	22.79	22.86	+0.3
,,	17.09	17.12	+0.2
,,	11.39	11.32	—0.6
		11.42	+0.3
,,	5.697	5.712	+0.3
		5.709	+0.2
		5.697	0.0
		5.697	0.0
,,	4.638	4.669	+0.7
Amperometric	17.09	17.09	0.0
		17.06	—0.2
,,	11.39	11.38	—0.1
		11.38	—0.1
,,	5.697	5.697	0.0
		5.692	—0.1
		5.687	—0.2
		5.681	—0.3
		5.688	—0.2
		5.692	—0.1
		5.708	+0.2
,,	4.638	4.659	+0.5
,,	2.319	2.314	—0.2

For amperometric end-point detection the e.m.f. impressed across the indicator electrodes was 150 mv, and the shape of the titration curve is shown in Fig. 4. Initially the indicator current is very small because the only possible reaction at the indicator anode is $2\,H_2O = O_2 + 4\,H^+ + 4\,e$, and the impressed voltage (150 mv)

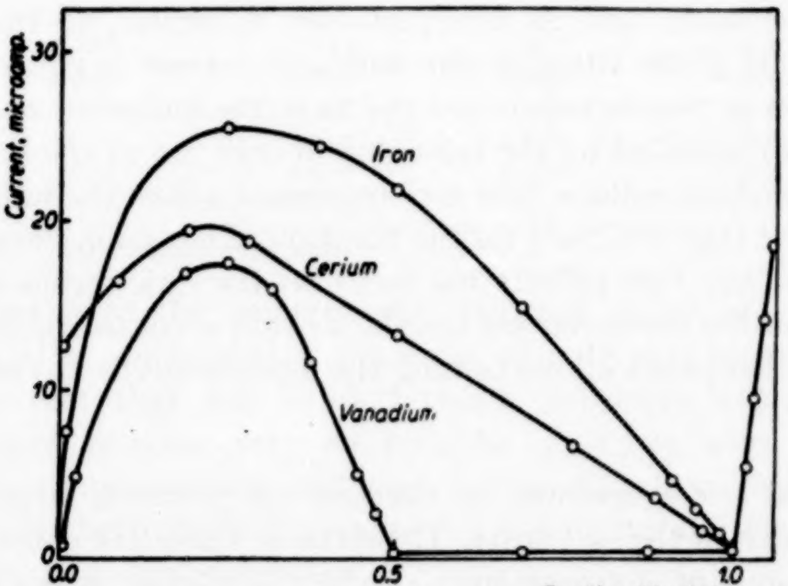

Fig. 4. Characteristics of amperometric titration curves. Approximately 10^{-4} moles were titrated at a rate of 25 milliamp. The applied voltage across the platinum indicator electrodes was: iron 150 mv; cerium, 500 mv; vanadium, 375 mv.

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is too small to cause this reaction to proceed at an appreciable rate. As soon as ferrous ion is produced the reactions at the indicator electrodes become

$$Fe^{+3} + e \rightarrow Fe^{+2} \text{ (cathode)}$$
$$Fe^{+2} \rightarrow Fe^{+3} + e \text{ (anode)}$$

and since the indicator electrodes become equivalent to a "concentration cell" of zero decomposition voltage the indicator current increases and attains a maximal value about half-way through the titration. During the first half of the titration the indicator current is governed by the rate of depolarization of the indicator anode by ferrous ion, and during the latter half by the rate of depolarization of the indicator cathode by ferric ion.

At the equivalence point the current is very small because in the virtual absence of ferric ion the only possible reaction at the indicator cathode is $Ti^{+4} \rightarrow Ti^{+3}$. Because the potential of the indicator anode is dictated by the reaction $Fe^{+2} \rightarrow Fe^{+3}$, and since the applied voltage is smaller than the difference in potential between the ferrous-ferric and titanic-titanous couples, the potential adopted by the indicator cathode is insufficiently reducing to cause reduction of +4 titanium at an appreciable rate.

When the equivalence point is passed, and +3 titanium is present, the indicator anode potential — now controlled by the reaction $Ti^{+3} \rightarrow Ti^{+4}$ — shifts to a much less oxidizing value. This displaces the potential of the cathode correspondingly to a value sufficiently reducing to cause reduction of +4 titanium, and consequently the current increases again. Less explicitly stated, the indicator electrode pair becomes equivalent to a titanic-titanous "concentration cell" of zero decomposition voltage.

In the neighborhood of the equivalence point the two branches of the indicator current-time curve closely approach linearity, and their intersection defines an end-point which differs only insignificantly from the equivalence point.

Cerium

Table II presents typical data obtained in the titration of +4 cerium.

The shape of the amperometric titration curve of +4 cerium, shown in Fig. 4, is qualitatively the same, and its interpretation is similar, to that of ferric ion. During the first half of the titration the indicator current is governed by the rate at which cerous ion is transferred to/and reacts at/the indicator anode, and during the latter half it is controlled by the reduction of ceric ion at the indicator cathode.

Although the constant voltage (500 mv) impressed across the indicator electrodes was larger than that (150 mv) used for the titration of ferric ion the maximal current is considerably smaller. This reflects the fact that the ceric-cerous couple functions less reversibly than the ferric-ferrous couple, so that a considerable fraction of the applied voltage is dissipated in overcoming the overpotentials at the two electrodes.

Vanadium

The reduction of +5 vanadium by titanous ion proceeds stepwise first to the +4 state and finally to the +3 state. The data in Table III demonstrate that accurate determinations of +5 vanadium can be made using either of the two end-points, and either potentiometric or amperometric detection. Hence vanadium can be determined when present in either the +5 or +4 states, and mixtures of +5 and +4 vanadium can be analysed.

TABLE II

COULOMETRIC TITRATION OF CERIC ION

The supporting electrolyte (volume *ca.* 100 ml) consisted of 6 to 8*M* sulfuric acid and 0.3 to 0.6*M* titanic sulfate. Generating currents from 10 to 40 milliamp (current density 0.7 to 2.7 milliamp/cm²) were used, to provide titration times of 100 to 500 seconds.

End-point detection	*Ceric ion, mg* *Taken*	*Found*	*Error %*
Potentiometric	25.02	24.97	—0.2
,,	14.58	14.45	—0.9
		14.54	—0.3
		14.58	0.0
		14.57	—0.2
Amperometric	58.32	58.35	+0.1
,,	29.16	29.27	+0.4
		29.19	+0.1
		29.19	+0.1
,,	14.58	14.57	—0.1
		14.57	—0.1
		14.57	—0.1
,,	1.458	1.467	+0.6
		1.456	—0.2
		1.461	+0.3
		1.452	—0.4

TABLE III

COULOMETRIC TITRATION OF +5 VANADIUM

The supporting electrolyte (volume *ca.* 100 ml) consisted of 6 to 8*M* sulfuric acid and 0.3 to 0.6*M* titanic sulfate. Generating currents from 15 to 25 milliamp (current density 1 to 1.7 milliamp/cm²) were used, to provide titration times of 300 to 600 seconds.

End-point detection	*Vanadium, mg* *Taken*	*Found* *(1)*	*(2)*	*Error %* *(1)*	*(2)*
Potentiometric	4.347	4.339	4.351	—0.2	+0.1
		4.361	4.353	+0.3	+0.2
		4.329	4.336	—0.5	—0.3
Amperometric	10.36	10.36	10.34	0.0	—0.2
,,	5.100	5.110	5.011	+0.2	0.0
,,	4.347	4.342	4.346	—0.1	0.0
		4.346	4.346	0.0	0.0
		4.345	4.346	0.0	0.0
		4.318	4.326	—0.8	—0.5

(1) First end-point; (2) Second end-point.

The characteristics of the amperometric titration curve of +5 vanadium are shown in Fig. 4. The amperometric detection of both end-points is possible only in virtue of the fact that the V^{+5}-V^{+4} couple functions nearly reversibly but the V^{+4}-V^{+3} couple behaves very irreversibly. LINGANE AND MEITES[5] showed by polarographic measurements, and also by equilibration experiments with a silver reductor, that both the reduction of +4 vanadium and the oxidation of +3 vanadium require large overpotentials.

Up to the first end-point the reactions at the indicator electrodes are

$$VO_2^+ + e + 2\ H^+ \rightarrow VO^{+2} + H_2O \text{ (cathode)}$$
$$VO^{+2} + H_2O = VO_2^+ + 2\ H^+ + e \text{ (anode)}$$

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Up to the maximum the indicator current is controlled chiefly by the oxidation of vanadyl ion at the indicator anode, and between the maximum and the first end-point the reduction of pervanadyl ion at the indicator cathode controls the current. Because the constant applied voltage (375 mv) is too small to overcome the large overpotentials associated with the vanadyl-vanadic couple the indicator current remains nearly zero between the first and second end-points, and then increases beyond the second end-point as the indicator electrodes are depolarized by the Ti^{+4}-Ti^{+3} couple.

The irreversible behaviour of the V^{+4}-V^{+3} couple is analytically advantageous, not only for the analysis of mixtures of +5 and +4 vanadium but also for the analysis of mixtures of +5 vanadium and ferric iron. In the latter case, the first amperometric end-point corresponds to the sum of $Fe^{+3} \rightarrow Fe^{+2}$ and $VO_2^{+} \rightarrow VO^{+2}$, and the second to $VO^{+2} \rightarrow V^{+3}$.

ACKNOWLEDGEMENT

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SUMMARY

The current efficiency for the electrogeneration of +3 titanium at a platinum cathode in sulfuric acid and hydrochloric acid media has been evaluated as a function of generating current density, concentration of +4 titanium, and acid concentration. With 6 to 8*M* sulfuric acid containing 0.6*M* titanyl sulfate the generation of titanous ion is 100% efficient up to a current density of 3 milliamp/cm². With this medium ferric ion, ceric ion, and +5 and +4 vanadium can be titrated coulometrically with errors of about ±0.3% or less.

RÉSUMÉ

Le rendement du courant lors de la formation électrochimique du titane(III) à une cathode de platine, en une solution contenant de l'acide sulfurique ou de l'acide chlorhydrique, est fonction de la densité de courant, de la concentration en titane(IV) et de la concentration en acide. Avec l'acide sulfurique 6 à 8*M*, renfermant du sulfate de titanyle 0.6*M*, le rendement de courant pour la formation d'ions titane(III) est de 100% pour des valeurs de la densité de courant allant jusqu'à de 3 milliamp/cm². Dans un tel milieu, le fer(III), le cérium (IV) et le vanadium(V) et (IV) peuvent être titrés coulométriquement avec des erreurs d'environ ± 0.3% au maximum.

ZUSAMMENFASSUNG

Die Stromausbeute bei der elektrochemischen Bildung von Titan(III) an einer Platinelektrode in schwefelsäure- oder salzsäurehaltiger Lösung wurde als Funktion der Stromdichte, der Titan(IV)-Konzentration und der Säure-Konzentration ermittelt. In 6 bis 8*M* Schwefelsäure und in Gegenwart von 0.6*M* Titanylsulfat beträgt bei Stromdichten bis zu 3 mA/cm², die Stromausbeute bei der Bildung der Titan(III)-Ionen 100%. Hierauf gründet sich eine Methode mittels derer Eisen(III), Cer(IV) und Vanadium(V) und (IV) coulometrisch mit Fehlern von maximal ± 0.3% titriert werden können.

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ÉTUDE ANALYTIQUE DE LA NIOXIME
(Cyclohexanedionedioxime)
DOSAGE POLAROGRAPHIQUE DU NICKEL

par

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O. WALLACH et coll.[1] ont, les premiers, étudié la nioxime. Celle-ci forme, avec le nickel, un précipité rouge dont la structure est donnée par FERGUSON ET BANKS[3]. De nombreux travaux[2–10] ont été entrepris pour déterminer les propriétés de ce réactif, particulièrement utilisé dans le dosage du nickel et du palladium.

La nioxime est plus soluble dans l'eau que la diméthylglyoxime[11,12], par contre, la nickel-nioxime est moins soluble que la nickel-diméthylglyoxime, ce qui augmente la valeur analytique de la nioxime. La nioxime donne un précipité brunâtre avec le cobalt, plus soluble que son composé de nickel. Avec les ions ferreux, elle forme, en solution ammoniacale, un composé coloré en rouge-violet[13,14,24]. On peut doser gravimétriquement le palladium[15,16] et colorimétriquement le rhénium[17].

Préparation de la nioxime

La nioxime a été préparée dans nos laboratoires par M. D. FOKIANOS, d'après E. G. RAUCH, G. F. SMITH, C. V. BANKS ET H. DIEHL[18]. Le point de fusion du produit obtenu est de 186°. La microanalyse élémentaire a donné:

%C calculé	*%C trouvé*	*%H calculé*	*%H trouvé*	*%N calculé*	*%N trouvé*
50.67	50.7 50.49	7.09	7.03 6.92	19.72	19.61

La préparation de la nioxime par synthèse de la 2-isonitrosocyclohexanone-1 par l'action du nitrite d'alcoyle sur la cyclohexanone[19] est à déconseiller. Le composé, dit *puriss.* fourni par une maison de produits chimiques, et préparé de cette façon, a donné un point de fusion très inférieur et l'analyse élémentaire ne correspond pas à celle de la nioxime bien que ce réactif forme aussi un composé rouge insoluble avec le nickel.

Notations

Les divers états d'ionisation seront représentés par les expressions RH_4^{+2}, RH_3^+, RH_2, RH^-, R^{-2}, RH_2 étant la formule de la molécule de nioxime. Nous désignerons les concentrations par ( ) et les activités par [ ].

I. Étude pH-métrique de la nioxime, détermination des couples acide-base K_1 et K_2

Des diverses possibilités de dissociation de la nioxime, la pH-métrie n'en fait apparaître que deux, correspondant aux équilibres:

$$RH_2 \rightleftarrows RH^- + H^+ \quad (K_1)$$
$$RH^- \rightleftarrows R^{-2} + H^+ \quad (K_2)$$

contrôlés par les constantes K_1 et K_2. Celles-ci ont déjà été déterminées par C. V. Banks et A. B. Carlson[20] par spectrophotométrie. Ils ont obtenu

$$pK_1 = 10.6 \pm 0.2$$
$$pK_2 = 12.4 \pm 0.5$$

Titrage de solution basique de nioxime par une solution titrée d'acide chlorhydrique

Appareil utilisé: Beckmann H-2. — Electrode Beckmann No. 8990-90.

Nous avons titré, par l'acide chlorhydrique $10^{-1}M$; 20 ml d'une solution renfermant la nioxime à la concentration $2.5 \cdot 10^{-2}$ M et l'hydroxyde de sodium à la concentration $5 \cdot 10^{-2}M$. Les résultats sont portés sur la Fig. 1 et dans le Tableau I.

TABLEAU I

TITRAGE D'UNE SOLUTION BASIQUE DE NIOXIME PAR HCl

Secteur	*Nioxime*	*pH*	*ml HCl $10^{-1}M$*	*Secteur*	*Nioxime*	*pH*	*ml HCl $10^{-1}M$*
A	R^{-2}	12.25	0	D	RH^-/RH_2	10.35	7.50
		12.20	0.5			10.28	7.75
		12.1	1.0			10.20	8
		12.0	1.5			10	8.50
		11.95	2.0			9.7	9
B	R^{-2}/RH^-	11.85	2.5			9.5	9.25
		11.75	3.0			9.20	9.50
		11.65	3.5			8.95	9.60
		11.50	4.0				
		11.35	4.5				
		11.30	4.6			8.65	9.70
		11.25	4.7			8.45	9 80
		11.22	4.8			7.70	9.90
		11.20	4.9	E	RH_2	6.60	10
						5	10.1
C	RH^-	11.15	5.0			3.20	10.25
						2.80	10.50
		11.10	5.2	F		2.55	11
						2.35	11.50
		11.02	5.4	G		2.25	12
		11.0	5.5	H		2.10	13
		10.9	5.8	I		2	14
		10.85	6		RH_3^+	1.90	15
		10.65	6.5				
		10.55	7				
		10.45	7.25				

Calcul des constantes K_1 et K_2

Dans ce calcul, nous avons fait intervenir les activités. Pour fixer la valeur K_e (constante d'ionisation de l'eau), il a été tenu compte de la température et de la force ionique de la solution.

Les concentrations (R^{-2}) et (RH^-), nécessaires au calcul de la force ionique, ont été obtenues par approximations successives.

Calcul de K_2 au point A (voir Figure 1 et Tableau I)

Tenant compte du fait que nous sommes en présence d'ions R^{-2} et que nous faisons intervenir les activités, la formule de Brönsted s'exprime de la façon suivante:

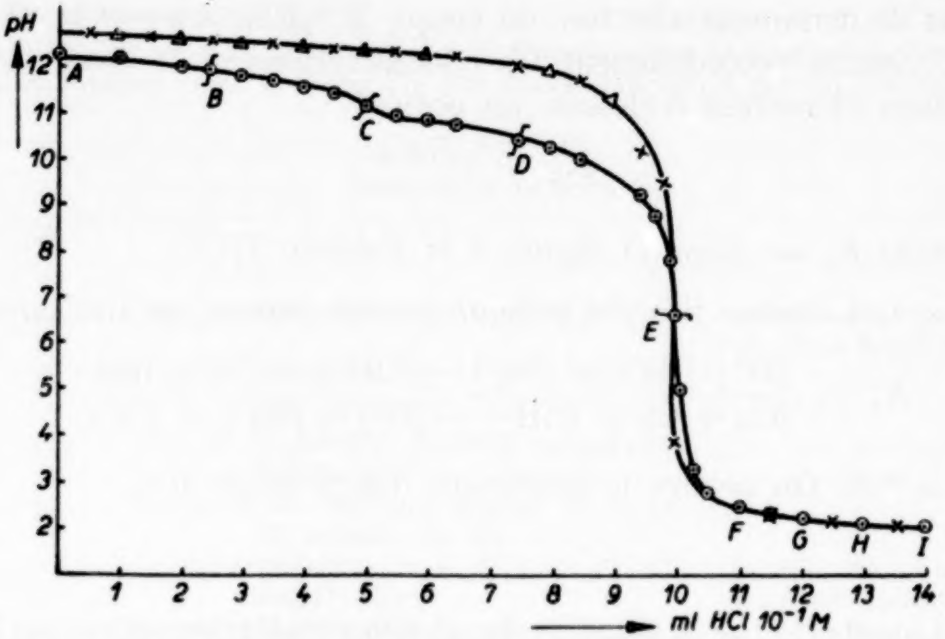

Fig. 1. ⊙ = Dosage des solutions de la nioxime $2.5 \cdot 10^{-2} M$ par HCl $10^{-1} M$
△ = Points calculés
× = Courbe de neutralisation de NaOH $10^{-1} M$ par HCl $10^{-1} M$

$$K_2 = \frac{[H^+]\ [(Na^+) + (H^+) - (OH^-) - Cb]\ f_{R^{-2}}}{[2\ Cb - (OH^-) - (Na^+) - (H^+)]\ f_{RH^-}}$$

dans laquelle () désigne les concentrations et [] les activités.

f_{RH^-} est le coefficient d'activité des ions RH^-
$f_{R^{-2}}$,, ,, ,, ,, ,, ,, R^{-2}
f_{OH^-} ,, ,, ,, ,, ,, ,, OH^-

Au point A, nous avons les concentrations suivantes:

$(Niox.)_{tot} = 2.5 \cdot 10^{-2} M$ $(RH^-) = 1.91 \cdot 10^{-2} M$
$(R^{-2}) = 5.9 \cdot 10^{-3} M$ $(Na^+) = 5 \cdot 10^{-2} M$ $[H^+] = 10^{-12.25}$

Les valeurs approximatives (R^{-2}) et (RH^-), nécessaires à la détermination de la force ionique, ont été obtenues au moyen des équations

$$\frac{(R^{-2}) \cdot [H^+]}{(RH^-)} = K_2 \text{ et } (R^{-2}) + (RH^-) = Niox._{tot}$$

en donnant à K_2 la valeur $10^{-12.7}$.

Dès lors, il est possible de calculer la force ionique. Nous admettrons 1 Å pour rayon des ions minéraux et 5 Å pour ceux de la nioxime. On obtient finalement pour la force ionique M = 0.054, au moyen de laquelle on calcule les coefficients d'activités

$f_{RH^-} = 10^{-0.09}$ $f_{H^+} = f_{Cl^-} = f_{OH^-} = 10^{-0.11}$
$f_{R^{-2}} = 10^{-0.355}$

En remplaçant ces diverses valeurs dans l'équation 1 on obtient:

$$K_2 = 10^{-12.67}$$

Détermination de K_2 au point B (Figure 1 et Tableau I)

La formule de Brönsted devient

$$K_2 = \frac{[H^+]\ [(Na^+) + (H^+) - (Cl^-) - Ca - Cb - (OH^-)]\ f_{R^{-2}}}{[2\ Ca + 2\ Cb - (Na^+) + (Cl^-) - (H^+) + (OH^-)]\ f_{RH^-}}$$

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En ce point de demi-neutralisation du couple R^{-2}/RH^-, $Ca = Cb = 1.11 \cdot 10^{-2} M$. En calculant comme précédemment les concentrations et la force ionique et en remplaçant dans l'équation ci-dessus, on obtient:

$$K_2 = 10^{-12.69}$$

Détermination de K_1 au point D (figure I et Tableau I)

Le calcul se fait comme il a été indiqué précédemment, en utilisant la formule

$$K_1 = \frac{[H^+]\ [(H^+) + (Na^+) - (OH^-) - (Cl^-)]\ f_{RH^-}}{[Ca + Cb + (OH^-) - (H^+) - (Na^+) + (Cl^-)]}$$

d'où $K_1 = 10^{-10.43}$. On néglige le coefficient d'activité de RH_2.

Remarques

Nous avons aussi effectué la titration de solutions acides de nioxime par l'hydroxyde de sodium, les constantes obtenues à partir de ces courbes sont très proches des valeurs données ci-dessus. D'autre part, il faut signaler que la formule approchée $[H^+] = \sqrt{K_1 \cdot K_2}$ ne s'applique pas ici. Celle proposée par DEFORT[21] donne avec nos valeurs $[H^+] = 10^{-11.3}$ qui se rapproche sensiblement de la valeur expérimentale (Figure 1, point C, pH = 11.15). Il faut souligner que la formule de DEFORT est approchée en ce sens qu'elle ne tient pas compte des activités.

En résumé, les erreurs les plus importantes proviennent de la mesure du pH. Si on admet que celles-ci sont de ± 0.05 pH, on peut calculer les écarts maximums, ce qui nous donne

$$pK_2 = 12.7 \pm 0.3 \qquad pK_1 = 10.4 \pm 0.2$$

Ces résultats sont très proches de ceux donnés par spectrophotométrie, bien que BANKS ET CARLSON ne fassent pas mention des activités.

II. Étude polarographique de la nioxime

P. SOUCHAY ET S. SER[22] ont examiné le comportement polarographique d'un certain nombre d'oximes et dioximes sans toutefois étudier la nioxime. Z. VODRÁŽKA[23] a entrepris l'étude de dérivés de l'hydroxylamine, en particulier de la cyclohexanedionedioxime. Enfin M. ISHIBASHI et coll.[24], CALZOLARI ET FURLANI[25] ont proposé une méthode ampérométrique de dosage de nickel par la nioxime après avoir recherché quelques propriétés polarographiques de cette dernière. Nous nous sommes attachés à l'étude de ce réactif afin de déterminer le produit de solubilité de la nickel-nioxime d'une part et de mettre au point un dosage polarographique du nickel d'autre part. Nous signalerons quelques petites divergences avec les deux derniers auteurs cités en ce qui concerne le comportement polarographique de la nioxime.

Appareillage et conditions expérimentales

Polarographe Sargent XIX, pH-mètre Beckman No. 8990-90.
Temps de goutte 4 sec.
Masse d'une goutte de mercure 0.2 mg
Hauteur du mercure h = 30 cm.

Dans l'ensemble des polarogrammes, on distingue trois sauts que nous désignerons par les symboles H_I, H_{II} et H_{III}, dans l'ordre des potentiels croissants.

Préparation des solutions

Dans un ballon jaugé de 50 ml on introduit 5 ml d'une solution de nioxime $10^{-2} M$ et on complète avec la solution tampon (voir Tableau II). On chasse l'oxygène par un courant d'hydrogène.

TABLEAU II

SOLUTIONS TAMPON

pH		
2	50 ml KCl $M/5$ + 10.6 ml HCl $N/5$	dilué à 200 ml avec de l'eau bidistillée
3	50 ml biphtalate K $M/5$ + 20.5 ml HCl $N/5$	,,
4	50 ml biphtalate K $M/5$ + 0.4 ml NaOH $N/5$	,,
5	0.059 M ac. acétique glacial + 0.141 M acétate de Na	—
6	50 ml biphtalate de K $M/5$ + 46 ml NaOH $N/5$	dilué à 200 ml avec de l'eau bidistillée
7	50 ml KH_2PO_4 $M/5$ + 30 ml NaOH $N/5$	,,
8	50 ml H_3BO_3 $M/5$ + 4 ml NaOH $N/5$	,,
9	50 ml H_3BO_3 $M/5$ + 21.3 ml NaOH $N/5$	,,
10	50 ml H_3BO_3 $M/5$ + 43.9 ml NaOH $N/5$	,,
11	51 ml glycine + 49 ml NaOH $N/10$	—
12	45 ml glycine + 55 ml NaOH $N/10$	—

Étude polarographique de la nioxime à divers pH

Les résultats sont donnés dans le Tableau III, et la Fig. 2.

TABLEAU III

RÉSUMÉ DES RÉSULTATS POLAROGRAPHIQUES DE LA NIOXIME

pH		*Micro-ampères*		*Saut*	*n*
	H_I	H_{II}	H_{III}	*tot.*	*tot.*
2.05	1.40	22	—	23.4	8
3	—	25	—	25	8
4	—	25	—	25	8
5	—	23	2	25	6
6	—	13.6	5.4	19	6
7	—	11.2	7	18.2	6
8.05	—	7.6	9.4	17.0	6
9	—	2.2	15	17.5	6
10	—	—	17.4	17.4	6
11	—	—	17	17	5
12	—	—	13.4	13.4	4

L'acidité favorise la formation du saut H_I et l'alcalinité le saut H_{III}. Le saut H_{II} est présent en milieu acide et jusqu'au pH 9. En milieu acide, nos résultats ne sont pas semblables à ceux des auteurs déjà cités[24,25]; il est vrai que nous n'utilisons pas les mêmes tampons que CALZOLARI et coll. et que les températures sont différentes. Il faut aussi tenir compte du fait qu'en milieu acide la solution évolue, nous le montrons à la page 481. Par contre, le point d'intersection des courbes H_{II} et H_{III} en fonction du pH (Fig. 2) se produit également au pH d'environ 7.7 trouvé par CALZOLARI.

Il est bien difficile d'expliquer l'origine des trois vagues. On pourrait supposer qu'elles sont dues aux particules RH_2, RH^- et R^{-2}. Dans ce cas, l'intersection des courbes permettraient de calculer les constantes des couples acide-base K_1 et K_2. Or, nous ne retrouvons pas les valeurs obtenues par pH-métrie et par spectrophotométrie et si l'on établit les courbes théoriques, on constate qu'elles sont absolument différentes de celle obtenue à la Fig. 3: courbe en traits pleins. Nous ne pouvons donc pas savoir quelles sont les particules qui, en se réduisant, donnent naissance aux diverses ondes observées. On constate pourtant que lorsque la vague I diminue, la vague II augmente et qu'à partir de pH 4, les hauteurs H_{II} diminuent au profit de H_{III}. Peut-être faudrait-il faire intervenir les courants cinétiques? Nous nous proposons de faire une étude du comportement polarographique de la nioxime à divers pH et à diverses températures.

Détermination du nombre d'électrons n

La réaction n'étant pas réversible, le calcul de *n* ne peut se faire à partir de l'équation de Nernst. Nous avons donc comparé le saut de la nioxime à celui connu de la benzophénone dont la structure est assez proche de celle de la nioxime et dont on sait que la réaction sur l'électrode fait intervenir au pH 6.85 deux électrons par réduction en benzhydrol [22,26]. Le Tableau IV donne les résultats des hauteurs des vagues de la nioxime. Les valeurs de *n* ont été calculées à partir du saut de la benzophénone de même concentration ($10^{-3}M$) dont la hauteur est de 6.4 μA.

TABLEAU IV

pH	*3*	*4*	*5*		*6*		*7*		*8*		*9*		*10*	*11*	*12*
Vague	II	II	II	III	II	III	II	III	II	III	II	III	III	III	III
HμA	25	25	23	2	5.5	13.8	7	11.2	9.8	7.4	15	2.2	18	17	13.5
n'	7.84	7.84	7.84		6.2		5.72		5.4		5.4		5.6	5	4.2
n	8	8	8		6.3		5.83		5.5		5.5		5.7	5.1	4.3

Ainsi, après les corrections nécessaires dues au fait que le coefficient de diffusion des deux composés n'est pas absolument identique, on remarque qu'en milieu acide et jusqu'au pH 5 la réaction fait intervenir 8 électrons, ce qui implique que la réduction

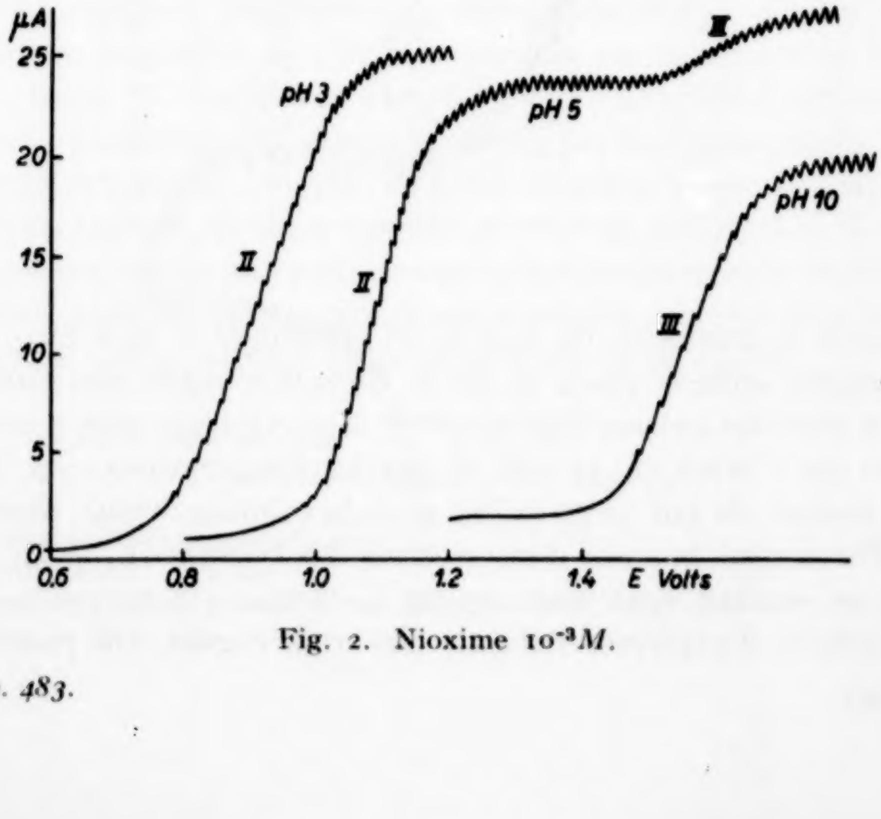

Fig. 2. Nioxime $10^{-3}M$.

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de la nioxime va jusqu'à la diamine, phénomène déjà observé par maints auteurs. La réduction est moins poussée en milieu alcalin. ISHIBASHI et coll. ont aussi déterminé ce nombre d'électrons et l'ont trouvé égal à huit mais en milieu alcalin. Comme la hauteur des sauts est plus élevée en milieu acide, il faudrait donc admettre que dans ces conditions de pH la réduction dépasse le stade amine.

III. Détermination du produit de solubilité (Ps) de la nickel-nioxime

Pour cette détermination, qui est délicate car ce complexe est très peu soluble, nous avons fait appel aux mesures pH-métrique et polarographique.

Méthode pH-métrique. Le produits de solubilité a été obtenu en déterminant le pH de précipitation de la nioxime de nickel au moyen du pH-mètre Beckmann, en procédant de la façon suivante: on ajoute, au moyen d'une microburette, une solution d'hydroxyde de sodium titrée à une solution renfermant en partie équimoléculaire de la nioxime et des ions Ni^{+2} jusqu'à apparition d'un précipité. Les résultats sont parfaitement reproductibles. Nous avons effectué deux séries de détermination avec deux concentrations différentes de nioxime et de nickel.

Première série. La solution est composée de:

1 ml de nioxime $5 \cdot 10^{-2} M$
10 ml de HCl $10^{-1} M$
0.5 ml de $NiCl_2$ $5 \cdot 10^{-2} M$.

Au début, la solution est parfaitement claire, puis elle rosit et le complexe précipite après addition de 0.2 ml de NaOH $10^{-1} M$, le pH est alors de 1.07.

Le produit de solubilité est calculé au moyen des formules suivantes:

$$[RH^-]^2 \cdot [Ni^{+2}] = Ps \qquad \frac{[H^+] \cdot (RH^-)}{(RH_2)} = 10^{-10.4}$$

$$\text{Ni tot.} = (Ni^{+2}) + Ni\,(RH)_2$$
$$\text{Niox. tot.} = (R^{-2}) + 2\,(Ni(RH)_2) + (RH_2) + (RH^-)$$

Nous admettrons qu'au pH de précipitation la quantité de $(Ni(RH)_2)$ en solution est négligeable de même que (R^{-2}). Dans ces conditions, les concentrations sont:

$$\text{Niox. tot.} = 4.27 \cdot 10^{-3} M$$
$$\text{Ni tot.} = 2.14 \cdot 10^{-3} M$$

Par le fait que lors des calculs on obtient directement les activités $[RH^-]$ et $[H^+]$, il suffit de connaître le coefficient d'activité des ions $[Ni^{+2}]$.

$$\text{Force ionique } \mu = 9.7 \cdot 10^{-2} \quad f_{Ni^{+2}} = 10^{-0.564}$$

En reportant les valeurs ci-dessus dans les formules données on obtient comme valeur du produit de solubilité

$$Ps = 2.31 \cdot 10^{-27}$$

Deuxième série. Des déterminations identiques effectuées sur une solution renfermant 0.5 ml de nioxime $5 \cdot 10^{-2} M$, 10 ml de HCl $10^{-1} M$ et 0.25 ml de $NiCl_2$ $5 \cdot 10^{-2} M$ donnent un pH de précipitation de 1.45 après avoir ajouté 3.5 ml d'hydroxyde de sodium $10^{-1} M$.

Par des calculs analogues aux précédents, on obtient

$$Ps = 1.11 \cdot 10^{-27}$$

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Dans ces déterminations l'erreur principale provient de l'imprécision de la constante K_1 ($\pm$ 0.3) et de la mesure du pH ($\pm$ 0.05).

Si on cherche à estimer les erreurs maximums dont ces mesures sont entachées en faisant les calculs avec les valeurs extrêmes de K_1 et du pH, on obtient des variations de $\pm$ 0.5 ce qui donne

$$p^{Ps} = 26.6 \pm 0.5$$
$$p^{Ps} = 26.9 \pm 0.5$$

Méthode polarographique

Nous sommes partis du précipité de nickel-nioxime, préparé en faisant réagir des solutions équimoléculaires de chlorure de nickel et de nioxime. Le précipité est filtré et soigneusement lavé avec de l'eau distillée. Il est maintenu humide. Nous avons constaté en effet que le séchage à 95° provoque d'importantes modifications de la solubilité.

Le principe de la méthode consiste à traiter la nickel-nioxime solide en excès par une solution aqueuse de pH déterminé.

On a:

$$(\mathrm{RH})_2\mathrm{Ni} + 2\,\mathrm{H}^+ = 2\,\mathrm{RH}_2 + \mathrm{Ni}^{+2}$$

On élimine l'excès du précipité par centrifugation et on détermine au polarographe la nioxime solubilisée. Cette détermination a été faite à trois pH différents (2.0;1.8;1.6) obtenus par addition d'acide chlorhydrique.

Nous avons établi dans les mêmes conditions le polarogramme d'une solution de nioxime $10^{-3}M$. Il est ainsi aisé de comparer les sauts et de déterminer la quantité de nioxime solubilisée. Dans tous les cas nous avons ajouté 2 gouttes de tylose à 0.5% (suppresseur de max.). Au pH supérieur ou égal à 1.8, le saut provenant de la dissolution du précipité est trop petit pour pouvoir être mesuré avec une certaine précision. Pour le pH 1.6 le saut du nickel est mal dessiné, aussi avons-nous calculé la concentration du nickel à partir de celle de la nioxime.

Au pH 1.6, nous avons:

Saut de la nioxime solubilisée $h_1 = 1.3\ \mu\mathrm{A}$
Saut de la solution de nioxime $10^{-3}M$ $h_2 = 8.8\ \mu\mathrm{A}$

d'où:

Conc. nioxime solubilisée $= 1.48 \cdot 10^{-4}$
Conc. de Ni^{+2} $= 0.74 \cdot 10^{-4}$

Le calcul du produit de solubilité se fait au moyen des formules suivantes:

$$\text{Niox. tot.} = (\mathrm{RH_2}) + (\mathrm{RH^-}) + (\mathrm{R^{-2}}) = 1.48 \cdot 10^{-4} \quad \ldots\ldots\ldots \quad (1)$$

$$\frac{[\mathrm{H^+}] \cdot [\mathrm{RH^-}]}{[\mathrm{RH_2}]} = K_1 \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

$$Ps = [\mathrm{Ni^{+2}}] \cdot [\mathrm{RH^{-2}}] \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

Dans l'équation 1 on peut négliger ($\mathrm{RH^-}$) et ($\mathrm{R^{-2}}$).

Les calculs donnent:

$$[\mathrm{RH^-}] = 2.34 \cdot 10^{-13}$$
$$(\mathrm{Ni^{+2}}) = 0.74 \cdot 10^{-3}$$
$$f_{\mathrm{Ni^{-2}}} = 0.5$$

d'où: $Ps = 2 \cdot 10^{-30}$ $\quad p^{Ps} = 29.7 \pm 0.7$

Les mêmes calculs effectués sur les valeurs obtenues pour le pH 1.8 donnent:

$$p^{Ps} = 30.64 \pm 0.9$$

Cette dernière valeur est très approximative car le saut de la nioxime est très mal dessiné.

Les résultats ci-dessus sont différents de ceux trouvés par la méthode potentiomé-

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trique mais ils ne sont pas comparables car dans le premier cas il s'agit de l'apparition du précipité alors que ces dernières valeurs sont obtenues par mise en solution du complexe.

IV. Dosage polarographique de la nioxime et du nickel

1. Stabilité de la nioxime

Avant d'établir une courbe d'étalonnage, nous nous sommes proposé d'étudier la stabilité de ce réactif à divers pH. Nous avions en effet constaté une évolution de la solution en milieu acide. La Figure 3 donne un aperçu de ce phénomène. Pour des pH inférieurs à 5, on observe un affaiblissement du saut II au profit du saut I. Par contre, à partir du pH 5, les solutions sont parfaitement stables pendant au moins 8 jours.

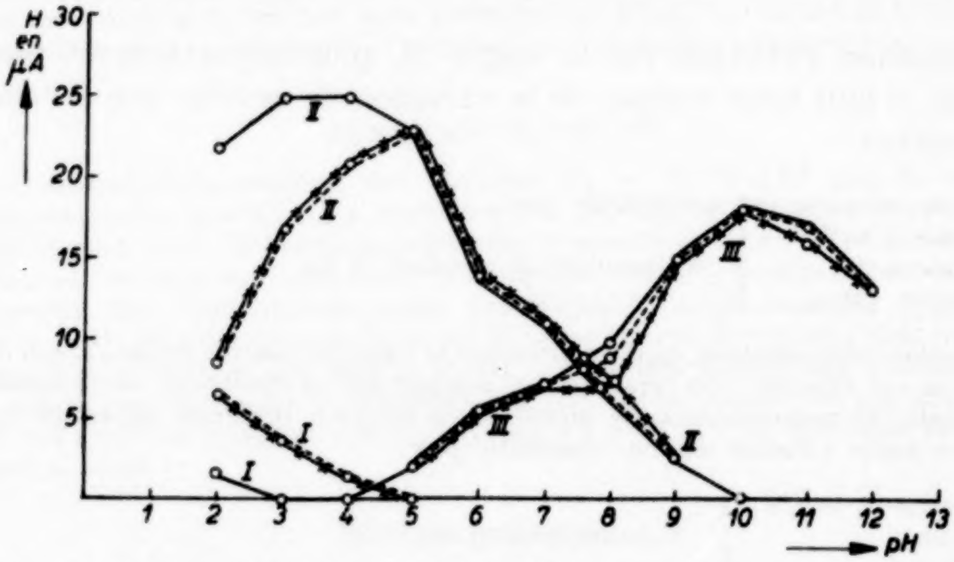

Fig. 3. Hauteur des vagues de la nioxime en fonction du pH et du temps.
premier jour = ————
deuxième jour = - - - - - - - - - - -
huitième jour = —×—×—×—×—×

2. Dosage de la nioxime

L'étude de la Figure 3 montre un maximum de stabilité des solutions de nioxime aux pH 5, 6 et 10. D'autre part, aux pH 5 et 10, les courbes sont particulièrement bien dessinées, aussi avons-nous conservé ces valeurs pour l'établissement des courbes d'étalonnage.

Au pH 5. Si on a soin de fixer la façon de mesurer la hauteur des sauts (méthode des tangentes par ex.) et d'établir deux courbes d'étalonnage, l'une pour des concentrations de nioxime comprises entre $10^{-3}M$ et $10^{-4}M$ l'autre pour des concentrations comprises entre $10^{-4}M$ et $10^{-5}M$, il est possible de doser ce composé avec une précision d'au moins 2% jusqu'à des concentrations de $5 \cdot 10^{-5}M$.

Quelques résultats sont donnés dans le Tableau V.

On peut donc doser 10 γ de nioxime dans 1 ml de solution.

Au pH 10.— Le dosage à ce pH est un peu moins précis et pour $4 \cdot 10^{-5}M$ l'erreur peut atteindre ± 7%.

3. Dosage polarographique du nickel

Ce dosage très simple est basé sur la détermination de la concentration de la nioxime avant et après addition de la solution inconnue de nickel. Le précipité de nickel-nioxime ne gêne pas, il n'est donc pas utile de le filtrer.

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TABLEAU V

Concentration molaire	*Hauteur théorique μA*	*Concentration trouvée*	*Hauteur trouvée μA*	*D*	*S $\mu A/mm$*	*Erreur %*
$8 \cdot 10^{-4}$	19.6	$8 \cdot 10^{-4}$	19.6	2	0.2	0
$2 \cdot 10^{-4}$	5.2	$1.9 \cdot 10^{-4}$	5.0	2	0.1	— 0.5
$5 \cdot 10^{-4}$	12.2	$5 \cdot 10^{-4}$	12.2	2	0.1	0
$5 \cdot 10^{-4}$	12.2	$5 \cdot 10^{-4}$	12.2	2	0.1	0
$7 \cdot 10^{-4}$	17	$6.9 \cdot 10^{-4}$	16.8	2	0.1	— 1.5
$7 \cdot 10^{-5}$	1.88	$7 \cdot 10^{-5}$	1.88	1	0.02	0
$5.8 \cdot 10^{-5}$	1.56	$5.9 \cdot 10^{-5}$	1.58	1	0.02	+ 1.5
$4.7 \cdot 10^{-5}$	1.26	$4.8 \cdot 10^{-5}$	1.28	1	0.02	+ 2
$2 \cdot 10^{-5}$	0.54	$2.2 \cdot 10^{-5}$	0.6	1	0.02	+ 10

La détermination s'effectue sur la vague II, plus importante et plus sélective. Dans le calcul, il faut tenir compte de la variation de volume due à l'addition de la solution de nickel.

La solution de nioxime est constitutée par:

1 ml de nioxime $5 \cdot 10^{-3} M$ 0.1 ml de tylose 0.5% 3.9 ml de tampon pH 5	Volume de la solution 5 ml

On polarographie cette solution, puis on introduit la solution connue de nickel qui doit renfermer de 24 à 210 γ de cet élément. On refait un polarogramme, la différence de la hauteur des sauts permet de calculer la concentration de nickel. Si la solution renferme moins de 24 γ de nickel on utilisera une autre solution étalon constituée par:

0.5 ml de nioxime $5 \cdot 10^{-3} M$ 0.5 ml de tylose 4.3 ml de tampon	Volume total 5 ml

Dans le Tableau VI nous donnons quelques résultats obtenus par cette méthode:

TABLEAU VI

Saut II μA	*γ de nickel théorique*	*γ de nickel trouvé*	*Erreur %*
22	45	45	0
19.9	76	78	+ 2.5
13.5	180	175	— 2
10.7	15.3	15	— 2
9.7	20.5	21	+ 2
9.35	24.5	23	— 6
7.95	32	31.5	— 1.5
7.2	35	35.8	+ 2.5

La précision du dosage est de ± 2% pour une quantité de nickel de l'ordre de 6 γ par ml, elle passe à ± 4% pour une quantité de nickel de 0.6 γ par ml.

Pour plus de détails consulter Thèse W. Bachmann[27].

RÉSUMÉ

Nous avons déterminé par potentiométrie les deux constantes de dissociation de la nioxime $K_2 = 10^{-12.6 \pm 0.3}$ et $K_1 = 10^{-10.4 \pm 0.3}$. Le comportement de la nioxime en fonction du pH et du temps est examiné et une méthode de dosage établie. Il est possible de doser la nioxime avec une précision de 2% jusqu'à la concentration de $5 \cdot 10^{-3}$.

D'autre part nous avons déterminé le produit de solubilité de la nickel-nioxime, potentiométri-

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quement $Ps = 10^{-27}$ et polarographiquement $Ps = 10^{-30}$. Ces deux valeurs ne sont pas comparables, l'une étant obtenue par précipitation du complexe, l'autre par la mise en solution de ce dernier.

Une méthode de dosage du nickel est mise au point; elle permet de doser 6 γ de nickel dans 1 ml avec une précision de ± 2%, 0.6 γ de nickel dans 1 ml avec une précision de ± 4%.

SUMMARY

By means of potentiometry we have determined the two dissociation constants of nioxime $K_2 = 10^{-12.6 \pm 0.3}$ and $K_1 = 10^{-10.4 \pm 0.3}$. The behaviour of nioxime as a function of pH and time has been investigated and a method of determination established. It is possible to determine the nioxime with an accuracy of 2% up to a concentration of $5 \cdot 10^{-3}$.

We have determined the solubility product of nickel-nioxime; potentiometrically $Ps = 10^{-27}$ and polarographically $Ps = 10^{-30}$. These two values are not comparable, the one being obtained by precipitation of the complex, the other by dissolving the complex.

A method of determining nickel has been perfected by which 6 γ nickel in 1 ml can be determined with an accuracy of ± 2% and 0.6 γ nickel in 1 ml with an accuracy of ± 4%.

ZUSAMMENFASSUNG

Die beiden Dissoziationskonstanten des Nioxims $K_2 = 10^{-12.6 \pm 0.3}$ und $K_1 = 10^{-10.4 \pm 0.3}$ wurden potentiometrisch ermittelt. Das Verhalten des Nioxims in Funktion des pH und der Zeit wurde untersucht und eine Bestimmungsmethode ausgearbeitet, mittels welcher das Nioxim in Konzentrationen bis zu $5 \cdot 10^{-3}$ mit einer Genauigkeit von 2% bestimmt werden kann.

Anderseits wurde das Löslichkeitsprodukt des Nickel-Nioxims ermittelt; potentiometrisch findet man $Ps = 10^{-27}$, polarographisch $Ps = 10^{-30}$. Diese beiden Werte sind aber nicht vergleichbar, da der eine durch Fällung, der andere durch Lösung des Komplexes erhalten wurde.

Schliesslich wurde eine Methode zur Bestimmung von Nickel ausgearbeitet, mit welcher man 6 γ Ni in 1 ml mit einer Genauigkeit von ± 2% und 0.6 γ Ni in 1 ml mit einer Genauigkeit von ± 4% bestimmen kann.

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SOME APPLICATIONS OF THE DIFFERENTIAL GALVANOMETER IN POLAROGRAPHY

by

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I. INTRODUCTION

As far as known to us, only HEYROVSKÝ[1,3] and KIES AND NIJON[2] have ever pointed out the importance of the differential galvanometer for recording derivative polarograms. However, this instrument is useful also for damping oscillations and for recording differential polarograms.

For those cases where derivative plots present certain advantages over normal current-voltage curves it was felt necessary to know the behaviour of the peak height as a function of the concentration of the electro-active substance concerned, the resistance of the cell-circuit and other variables. For, the practical usefulness of this method depends on the degree to which the relation between peak height and concentration deviates from linearity.

II. EXPERIMENTS AND INTERPRETATION

1. In general oscillations are — if necessary — damped by means of electrolytic condensers. In some cases this may give rise to disturbance of the polarographic picture owing to the sudden occurrence of leakage currents. By short circuiting coil *II* by means of *S* (see Fig. 1) oscillations can be damped by means of the adjustable resistance *R*, without any disturbance.

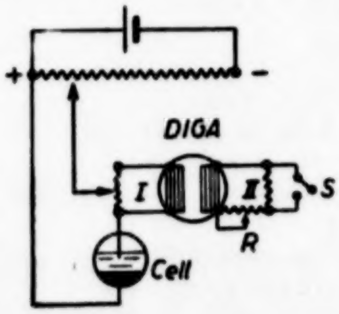

Fig. 1. Diagram of a circuit used for damping oscillations; DIGA: differential galvanometer*, *S* : switch, *R* : adjustable resistance 5500 Ω.

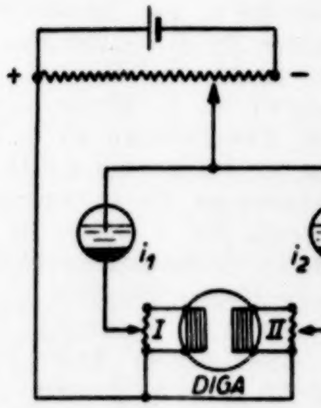

Fig. 2. Diagram for differential polarography.

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* DIGA, made by Kipp, Delft (Holland), type A 62, with some alterations: the galvanometer can be critically damped by means of a 5000 Ω Ayrton-shunt, in which case the time of indication is about 10 sec. The sensitivity is about $2 \cdot 10^{-10}$ A/mm/m. The diameter of the mirror was enlarged to 8 mm.

2. The differential galvanometer may be very useful also in differential polarography (see Fig. 2). This figure is a simplification of the scheme originally drawn up by SEMERANO AND RICCOBONI[5]; furthermore the interpretation of the differential polarogram is now very simple, provided the resistances of the two cell circuits are equal and the two electrodes have the same capillary characteristics and are knocked off mechanically at the same time[4]. The two Ayrton-shunts *I* and *II* are coupled.

3. The most important use of the differential galvanometer is its application in derivative polarography[2] (Fig. 3), by which the circuit originally drawn up by HEYROVSKÝ[1,3] can be greatly simplified.

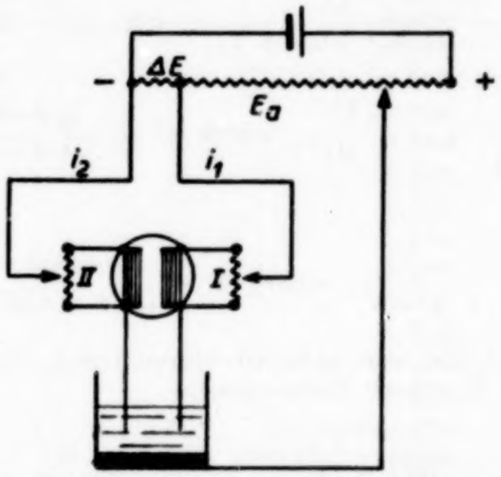

Fig. 3. Diagram for derivative polarography.

Between two dropping mercury electrodes with the same capillary characteristics, which are simultaneously knocked off, there is a small, constant potential difference, $\triangle E$. The two Ayrton-shunts *I* and *II* are also coupled. The resistance of cell circuit 1, R_1, (applied voltage E_a) will, in the symmetrical arrangement shown in Fig. 3, be equal to the resistance of cell circuit 2, R_2 (applied voltage $E_a + \triangle E$) and may consequently be represented by R. If the height of the mercury level over the first capillary is equal to the height over the second, i_{d_1} will be equal to i_{d_2} and so can be represented by a single symbol, i_d. By means of the differential galvanometer we measure $(i_2 - i_1)$ against E_a. We shall now examine the relation between the measured maximum value of $(i_2 - i_1) = i_m$ and the concentration of the electro-active substance causing this maximum, which concentration is proportional to i_d.

Omitting the sign of E_a and $\triangle E$, we get:

$$E_a = -(e_{d.m.e._1} - e_{s.c.e.}) + i_1R = -E_1^* + i_1R \text{ and}$$
$$E_a = -(e_{d.m.e._2} - e_{s.c.e.}) - \triangle E + i_2R = -E_2^* - \triangle E + i_2R,$$

where $e_{d.m.e.}$ = potential of the dropping mercury electrode (*d.m.e.*) and $e_{s.c.e.}$ = potential of the saturated calomel electrode, both measured with respect to the normal hydrogen electrode. If we now put $E_i = f(i) = E^* - E_{\frac{1}{2}}$, in other words: if we select the half-wave potential as reference potential, then it is possible to form the following equation for the reduction of an oxidation agent (red OX) (no RED is present):

$$E_{i_1} = E + i_1R = -\frac{1}{k} \ln \frac{i_1}{i_d - i_1} \quad \ldots\ldots\ldots\ldots \text{(1a) or:}$$

$$i_1 = \frac{i_d}{(e^{k(E + i_1R)} + 1)} \quad \ldots\ldots\ldots\ldots \text{(1b)}$$

and:

$$E_{i_2} = E - \triangle E + i_2R = -\frac{1}{k} \ln \frac{i_2}{i_d - i_2} \quad \ldots\ldots\ldots\ldots \text{(2a) or:}$$

$$i_2 = \frac{i_d}{(e^{k(E - \triangle E + i_2R)} + 1)} \quad \ldots\ldots\ldots\ldots \text{(2b)}$$

where $E = -E_a - E_{\frac{1}{2}}$ and $k = \dfrac{\alpha nF^{**}}{\mathbf{R}T}$.

** $k = \dfrac{\alpha nF}{\mathbf{R}T}$; α is the transmission coefficient, which is about 0.5 for irreversible reactions and 1 for reversible reactions. **R** is expressed in joule °K$^{-1}\cdot$mol^{-1}; T in °K; E in V; and i in A; so that $k = \alpha \cdot n \cdot 39.6$, at 20°C. So: $k = 20$: irreversible reaction with $n = 1$; $k = 40$: irreversible reaction with $n = 2$ or reversible reaction with $n = 1$, $k = 80$: reversible reaction with $n = 2$.

From this it follows that:

$$(i_2 - i_1) = i_d \left[\frac{1}{(e^{k(E - \triangle E + i_2R)} + 1)} - \frac{1}{(e^{k(E + i_1R)} + 1)} \right] \ldots\ldots\ldots \quad (3)$$

If now $(i_2 - i_1) = i_m$, then $\frac{\mathrm{d}(i_2 - i_1)}{\mathrm{d}E} = 0$, or $\frac{\mathrm{d}i_2}{\mathrm{d}E} = \frac{\mathrm{d}i_1}{\mathrm{d}E}$ .... (4)

We consider k, $\triangle E$ and R as being constant and write instead of (2b):

$$i_2 - \frac{i_d}{(e^{k(E + \mathrm{f}(i_2))} + 1)} = \mathrm{f}(E, i_2) = 0,$$

where $\mathrm{f}(i_2) = i_2R - \triangle E$. Now:

$$\frac{\mathrm{d}i_2}{\mathrm{d}E} = - \frac{\delta f/\delta E}{\delta f/\delta i_2} = \frac{-U}{1 + RU}, \text{ where } U = \frac{i_d \cdot k \cdot e^{k(E - \triangle E + i_2R)}}{(e^{k(E - \triangle E + i_2R)} + 1)^2}$$

Likewise we find:

$$\frac{\mathrm{d}i_1}{\mathrm{d}E} = \frac{-V}{1 + RV}, \text{ where } V = \frac{i_d \cdot k \cdot e^{k(E + i_1R)}}{(e^{k(E + i_1R)} + 1)^2}.$$

According to (4), $U = V$. If, for the sake of convenience, $k(E + i_1R)$ is called X_1, and $k(E - \triangle E + i_2R)$ is called X_2, then, consequently:

$$\frac{e^{X_1}}{(e^{X_1} + 1)^2} = \frac{e^{X_2}}{(e^{X_2} + 1)^2} \text{ or:}$$

$$e^{(X_1 + X_2)} \cdot (e^{X_1} - e^{X_2}) = (e^{X_1} - e^{X_2}).$$

This holds for $X_1 = X_2$ (where $(i_2 - i_1) = 0$), and for $X_1 = -X_2$, where $(i_2 - i_1) = i_m$.

Consequently, we find:

$$E_m = \tfrac{1}{2} \left[\triangle E - (i_2 + i_1)R\right] \ldots\ldots\ldots \quad (5)$$

where E_m is the potential at the maximum. From (1b), (2b) and (5) it now follows that — independent of the value of R — at the maximum

$$(i_2 + i_1) = i_d \ldots\ldots\ldots \quad (6)$$

so that

$$E_m = \tfrac{1}{2} (\triangle E - i_dR) \ldots\ldots\ldots \quad (7)$$

Equation (3) can now be simplified to

$$i_m = i_d \left[\frac{1}{(e^{-X} + 1)} - \frac{1}{(e^{X} + 1)} \right] \text{ where } X = \tfrac{1}{2} k (\triangle E - i_mR), \text{ so that, finally:}$$

$$i_d = i_m \cdot \frac{e^X + 1}{e^X - 1} = i_m \cdot Y \ldots\ldots\ldots \quad (8)$$

Table I and Fig. 4 show $Y = \mathrm{f}(X)$. As k depends on the type of the electrode reaction and on temperature, the value of $\triangle E$ is previously fixed and R as well as i_m are measured, the value of i_d follows from (8). In measuring practice the point is to choose such a value of $\triangle E$ with a given R (which should be made as small as possible, for only if $R = 0$ is i_m a linear function of i_d and hence of concentration), that:

a. i_m is as great as possible as compared with i_d, in other words: the loss in sensitivity inherent in the derivative measurement is as small as possible;

b. in the usual concentration range (*e.g.* up to $10^{-3}M$) i_m is an approximately linear function of the concentration;

c. the reduction peak is not disturbed by a preceding or a following reduction.

Consequently, in a. and b. an optimum value of $\triangle E$ is required, which is limited by condition c. This may easily be seen by transforming (8) into

$$\triangle E = \frac{2}{k} \ln \frac{1 + a}{1 - a} + R \cdot a \cdot i_d \ldots\ldots\ldots \quad (9)$$

where $i_m = a \cdot i_d$ and $0 \leqslant a \leqslant 1$.

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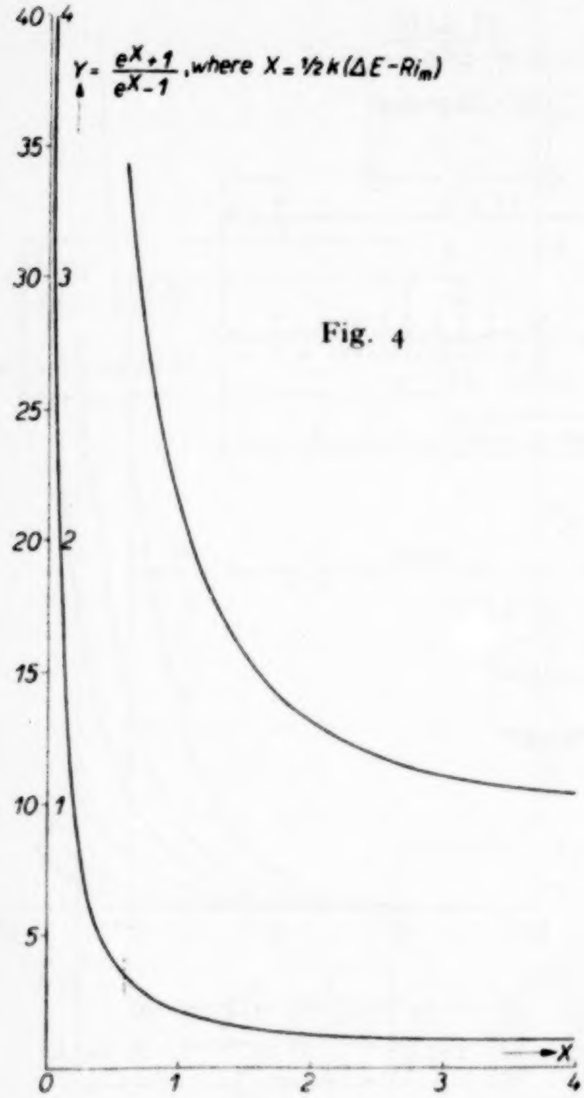


Fig. 4

TABLE I

X	Y
0.050	39.986
0.100	20.011
0.200	10.033
0.300	6.7159
0.400	5.0666
0.500	4.0830
0.600	3.4324
0.700	2.9729
0.800	2.6319
0.900	2.3702
1.000	2.1639
1.200	1.8620
1.400	1.6547
1.600	1.5059
1.800	1.3960
2.000	1.3130
2.200	1.2492
2.400	1.1995
2.600	1.1604
2.800	1.1294
3.000	1.1047
3.200	1.0850
3.400	1.0690
3.600	1.0561
3.800	1.0458
4.000	1.0373

Table II and Fig. 5 show the value of $\triangle E$ required at a desired accuracy-ratio a, at which k may have any of the values 20, 40 or 80 (according to the type of the electrode reaction), and at which the resistance of the cell circuit is negligible. Suitable values lie in most cases between 0.025 and 0.050 V. Now the danger of disturbance caused by a preceding or following reduction is not great. For, the width of the base of a reduction peak (see Fig. 6) is about equal to the width of the wave in a normal plot plus 2 $\triangle E$, in other words: the base of the peak is 2 $\triangle E$ wider. From (8) it follows that only i°_m, *i.e.* i_m at $R = 0$, is a linear function of the concen-

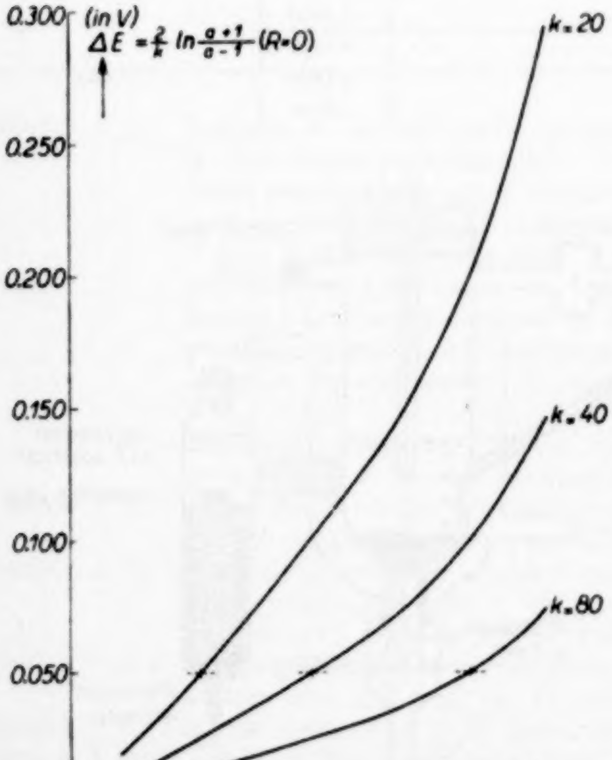


Fig. 5

TABLE II

a	ΔE in V at k = 20	40	80
0.10	0.020	0.010	0.005
0.30	0.062	0.031	0.016
0.50	0.110	0.055	0.027
0.70	0.173	0.087	0.043
0.90	0.294	0.147	0.074

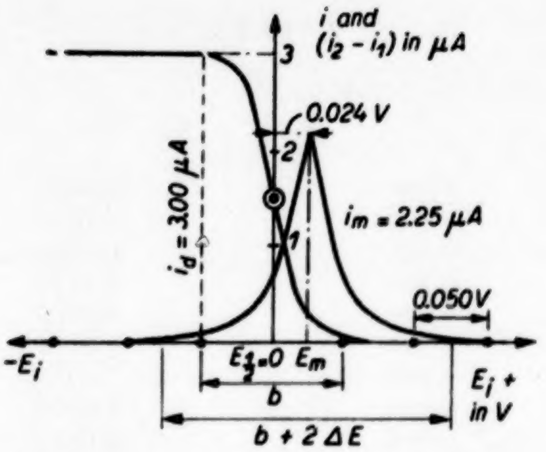


Fig. 6. Normal polarogram and derivative polarogram of $10^{-3}M$ maleic acid in $0.1M$ hydrochloric acid with 0.001% gelatin. $R = 500\,\Omega$ and $\triangle E = 0.050$ V.

tration. As a measure of the deviation of i_m we take:

$$f = \frac{i^\circ_m - i_m}{i^\circ_m} \cdot 100 = (1 - \frac{Y^\circ}{Y})\ 100 \quad (10)$$

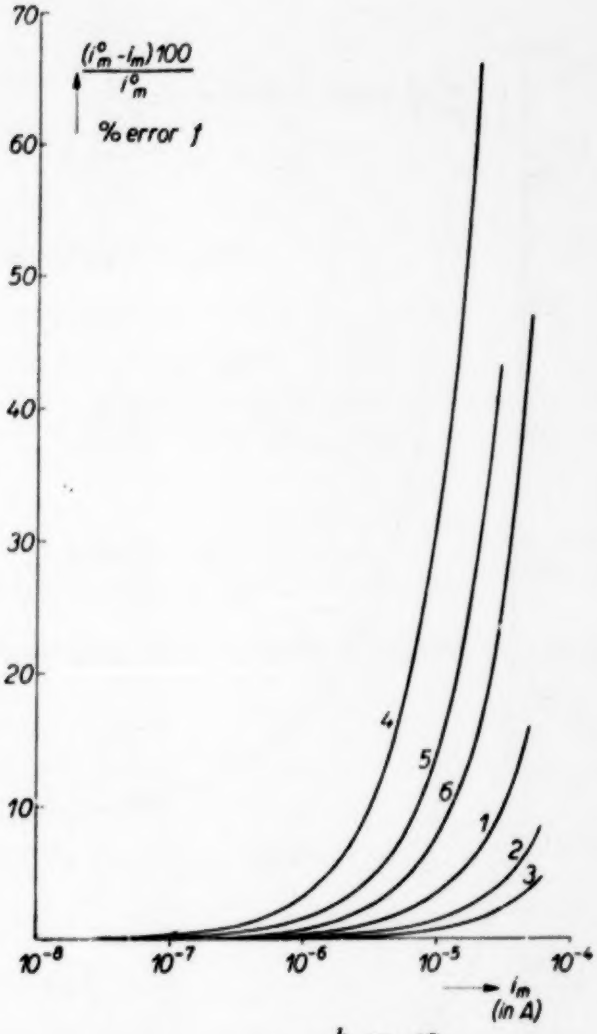
where

$$Y^\circ = \frac{e^{X^\circ} + 1}{e^{X^\circ} - 1} \text{ and } X^\circ = \tfrac{1}{2}k \triangle E.$$

Using Table 1 and Fig. 4 it is possible to determine very rapidly the deviation from linearity and — should this be necessary — to make a correction. For, $i^\circ_m Y^\circ = i_d = i_m Y$ or

$$i^\circ_m = i_m \frac{Y}{Y^\circ} \quad . \; . \; . \; . \; . \; . \; . \; (11$$

When the measuring results are interpreted the i_m found is converted, by means of (11), into i°_m. Fig. 7 shows the percentage error f plotted against the measured i_m for $k = 40$, if $\triangle E = 0.030$, 0.060 and 0.090 V, respectively, both for $R = 100$ and $1000\,\Omega$. This figure once more shows the importance of a low cell resistance and a not too small $\triangle E$. If a saturated calomel electrode (b) is preferred as reference counter-electrode to a pool of mercury on the bottom of the cell (a), a cell construction as illustrated in Fig. 8 may be used. With this arrangement the resistance of the cell circuit is reduced to a very low value, while — in spite of the compact construction — polarization of the reference electrode is confined to a minimum by the relatively large mercury surface. Fig. 9 is a diagram of a combined polarograph. The legend briefly explains the operation of this instrument.



$k = 40$

Fig. 7	$\triangle E$ in V	R in Ω
1.	0.030	100
2.	0.060	
3.	0.090	
4.	0.030	1000
5.	0.060	
6.	0.090	

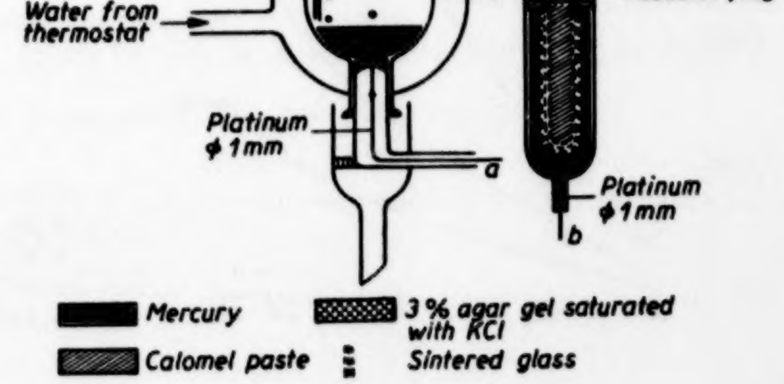


Fig. 8. Cell for derivative polarography. The two dropping mercury electrodes are placed behind each other and are hence symmetrically positioned with respect to the saturated calomel electrode ($R_1 = R_2 = R$).

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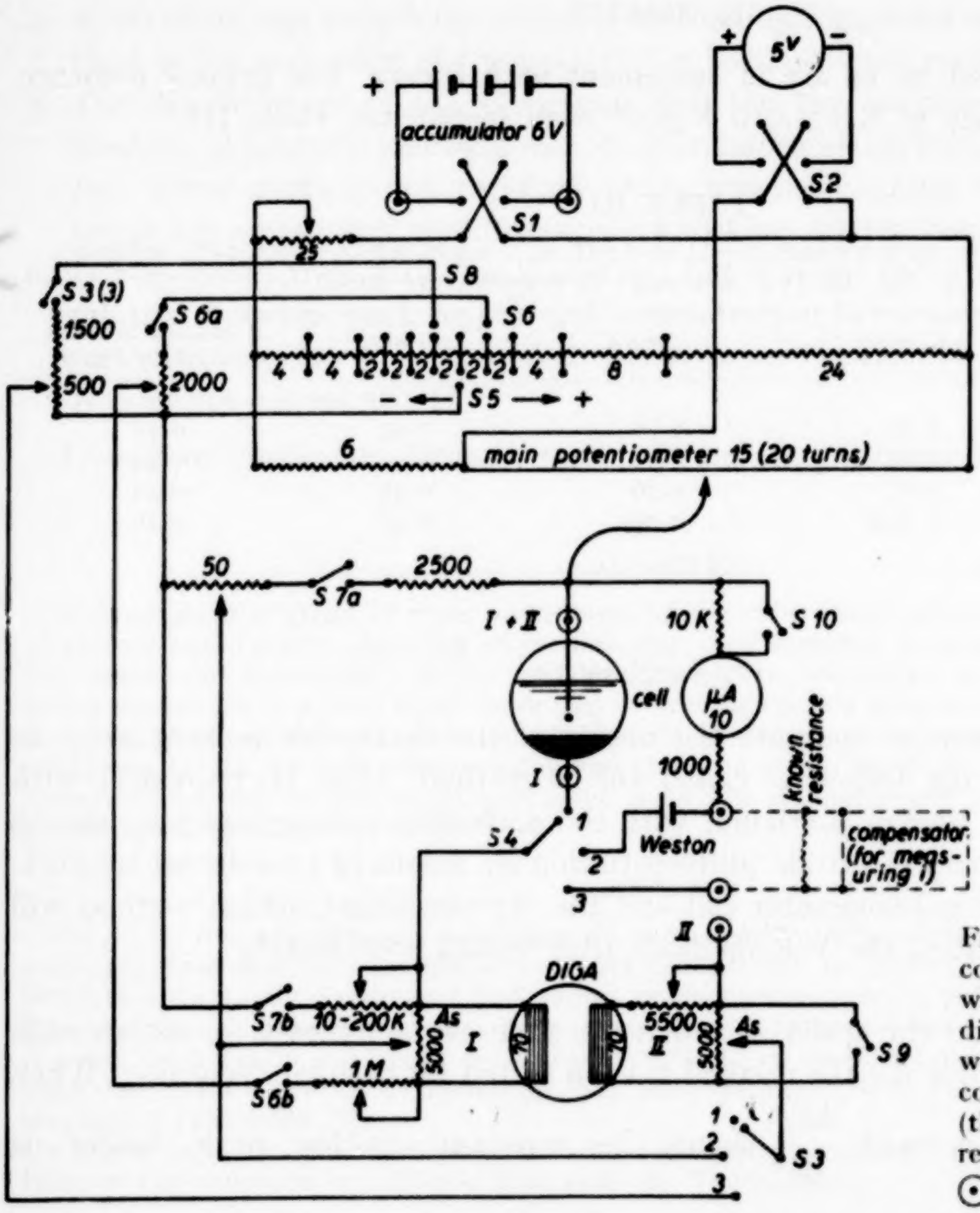
+
accumulator 6 V
−
+
5V
−
S1
S2
25
S8
S6
S 3(3)
1500
500
S 6a
2000
4
4
2
2
2
2
2
2
4
8
24
− ← S5 → +
6
main potentiometer 15 (20 turns)
50
S 7a
2500
I + II
10 K
S 10
cell
μA 10
1000
known resistance
I
S4
1
2
3
Weston
compensator (for measuring i)
II
DIGA
S 7b
10-200K
As
5000
I
70
70
5500
II
5000
As
S9
S 6b
1M
1
2
3
S3

Fig. 9. Diagram for a combined polarograph in which use is made of a differential galvanometer with photographic recording.
(the figures to the various resistances refer to ohms)
⊙ = connecting terminal.

Switch S 3:	position 1: normal polarography; position 2: differential polarography; position 3: derivative polarography. With position 3 coupled switches *S* 1 and *S* 2 from intermediate position upwards; potentiometer 5500 Ω (galvanometer coil II) in position 0. In position 3 switch *S* 3(3) is closed, *S* 9 is open.
Switch S 4:	position 1: connection to cell; position 2: calibration main potentiometer by means of Weston element and μA meter (previously adjusted as accurately as possible by means of potentiometer 25 Ω and voltmeter). Example: slide contact of main potentiometer in position 5.09, if the voltage is 0.200 V per turn (for, 5.09×0.200 V = 1.0183 V; 4 V across main potentiometer), correction by means of potentiometer 25 Ω; position 3: calibration of DIGA by measuring the voltage drop across a known resistance by means of a compensator.
Switch S 5:	adjustment of the starting potential (potential of the slide contact in position 0 with respect to the potential of the counter-electrode).
Switch S 6:	(direction) and the coupled switch *S* 6a, b serve to adjust the galvanometer at zero; potentiometers 1 MΩ and 2000 Ω serve for coarse and fine adjustment respectively. Out of action when *As I* has sensitivity 1.
Switch S 7a, b:	compensation of the condenser current, coarse and fine control with potentiometers 200 kΩ and 50 Ω respectively.
Switch S 8:	coarse control of $\triangle E$, fine control by means of potentiometer 500 Ω.
Switch S 9:	serves for the damping of oscillations in combination with potentiometer 5500 Ω (*S* 3 in position 1).
As:	Ayrton-shunt, sensitivity 1/1, 2/3, 1/2, 1/3, 1/5, 1/7, $1/1\cdot10^{-1}$, $2/3\cdot10^{-1}$.....$1/1\cdot10^{-4}$, $1/2\cdot10^{-4}$, $1/5\cdot10^{-4}$, $1/1\cdot10^{-5}$, $1/2\cdot10^{-5}$.

III. RESULTS

The results obtained by us are in agreement with theory. For greater evidence some measuring results of KIES AND NIJON[2] were tested, see Table III.

TABLE III

Lead solutions ($k = 80$, as $n = 2$ and $a = 1$) in $0.1M$ KCl, $0.2M$ KNO_3 and 0.01% gelatin; *R ca.* 600 Ω, $\triangle E = 0.0247$ V, temperature 20°C.

Concentration in mmol/l	i_m *in μA*	i_d *in μA*	*a found*	*a calculated by means of (9) see Fig. 5*
9.07	3.76	8.76	0.43	0.42
4.54	1.94	4.37	0.44	0.44
1.82	0.81	1.76	0.46	0.45
0.242	0.108	0.235	0.46	0.46

IV. DISCUSSION

It is an obvious step to compare the merits of the derivative polarography as discussed above (in the following called the H-method, after HEYROVSKÝ) with the classical method, and in particular with the derivative polarography by means of one dropping mercury electrode (differentiation by means of a condenser connected in series with the galvanometer coil and the Ayrton-shunt, which method will in the following be called the V-Ř-method, after VOGEL AND ŘÍHA[6]).

1. With the H-method the speed at which the slide contact moves is, within wide limits, not critical for i_m: the method is even suited for manual recording. When the V-Ř-method is used $\frac{dE_a}{dt}$ should be constant, as the peak height is proportional to it.
2. H-method: If $\frac{dE_a}{dt}$ is not too great, peak deformation occurs only if R becomes too great. With the V-Ř-method the peak is moreover subject to deformation on account of a recording lag of the galvanometer ($\frac{dE_a}{dt}$ should not be too small!) and a charging lag (the condenser should have a large capacity, as the peak height is proportional). These lags are difficult to account for mathematically. As a result of the peak deformation there are deviations from linearity in the relation between peak height and concentration.
3. With the H-method the oscillations occurring after the peak are so small as to be negligible, which is not the case if the V-Ř-method is used, see Fig. 10.

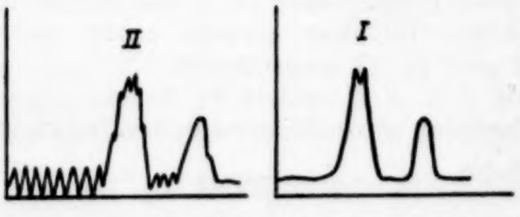

Fig. 10. Diagrams made by the H-method (I) and the V-Ř-method (II).

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4. A disadvantage attaching to the H-method as compared with the classical method is the wide base of the peak if $\triangle E$ becomes too great.
5. The disadvantage of the H-method that the two dropping mercury electrodes must be absolutely identical may be eliminated by dividing a long capillary into two equal parts (equal capillary characteristics), taking care that the mercury levels are equal, and simultaneously knocking off the two mercury electrodes[4].
6. It was found that with the H-method but a slight deviation in linearity of the relation between peak height and concentration is obtained up to a reasonable concentration ($10^{-3}M$), provided ΔE remains between 0.025 and 0.050V, and R does not exceed $500\ \Omega$.

I want to thank DR. DEINUM for his stimulating interest in this work.

SUMMARY

A description is given of some advantages of the differential galvanometer in the recording of normal polarograms (damping of oscillations), in differential polarography (simplification of the SEMERANO-RICCOBONI circuit) and particularly in derivative polarography. The height of the maximum of a derivative curve (i_m) is determined as a function of the diffusion current (i_d) (and hence of the concentration), the potential difference between two dropping mercury electrodes ($\triangle E$), the cell resistance (R) and the type of the electrode reaction (k).
Directives for the derivative-polarographic recording technique are outlined and the method is compared with that of VOGEL-ŘIHA.

RÉSUMÉ

On décrit d'abord quelques avantages du galvanomètre différentiel pour l'enregistrement de polarogrammes normaux (amortissement des oscillations), la polarographie de différence (simplification du circuit SEMERANO-RICCOBONI) et particulièrement la polarographie différentielle. On détermine la hauteur du maximum d'une courbe différentielle (i_m) comme fonction du courant de diffusion (i_d) (donc de la concentration), de la différence de potentiel entre les deux électrodes à gouttes de mercure ($\triangle E$), de la résistance de la cellule (R) et du type de la réaction à l'électrode (k).
On donne enfin des directives pour la technique d'enregistrement de la polarographie différentielle et l'on compare la méthode avec celle de VOGEL-ŘIHA.

ZUSAMMENFASSUNG

Einige Vorzüge des Differentialgalvanometers bei der Registrierung normaler Polarogramme (Dämpfung der Oszillationen), für die Differenzpolarographie (Vereinfachung der SEMERANO-RICCOBONI-Schaltung) und speziell die Differentialpolarographie werden beschrieben. Die Höhe des Maximums einer Differentialkurve (i_m) wird als Funktion des Diffusionsstromes (i_d) — und deshalb der Konzentration — weiter als Funktion der Potentialdifferenz beider Quecksilbertropfelektroden ($\triangle E$), des Widerstandes (R) des Elektrolysengefässes, sowie der Art der Elektrodenreaktion (k) ermittelt.
Es werden Anleitungen zur Technik differentialpolarographischer Messungen gegeben. Die Methode wird mit derjenigen von VOGEL-ŘIHA verglichen.

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ÉTUDE DE LA PHÉNYL-2 OXINE ET DE SES CHÉLATES

IV. POLAROGRAPHIE DE LA PHÉNYL-2 OXINE

par

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Ouvrant souvent la voie à de nouvelles applications analytiques, l'examen polarographique d'un réactif organique présente en outre l'avantage, sur un plan plus théorique, d'apporter d'utiles renseignements sur le comportement de la molécule vis-à-vis de l'électrode à gouttes de mercure, et en particulier sur son mécanisme de réduction.

Notre étude[1,2] de la phényl-2 oxine a donc été complétée par un examen polarographique dont nous résumons ici les résultats.

L'appareil utilisé était un polarographe A.O.I.P. à inscription manuelle (système Du Bellay). Toutes les solutions étudiées étaient tamponnées, et avaient subi au préalable une désaération par barbotage d'un courant d'azote.

Milieu hydroalcoolique

Par suite du peu de solubilité[1] de la phényl-2 oxine, l'emploi systématique d'un milieu solvant permettant de travailler sur des concentrations suffisantes serait nécessaire pour pouvoir effectuer une étude polarographique complète en fonction du pH, analogue par exemple à celles de Stock[3] sur l'acide quinaldique, l'oxine ou l'acide quinoléine-8 carboxylique.

Nos expériences en milieu hydroalcoolique ne nous ont cependant pas conduits à des résultats très intéressants.

La Fig. 1 représente le polarogramme de la phényl-2 oxine à une concentration

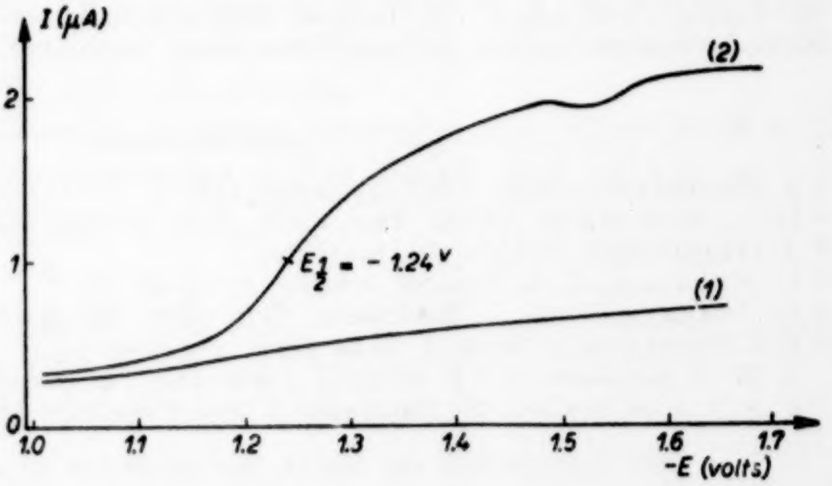

Fig. 1. Polarogramme de la phényl-2 oxine en milieu hydroalcoolique (30° G.L.), pH = 9.3.

1. Électrolyte support
2. Phényloxine C = 50 mg/l

Sensibilité: $16 \cdot 10^{-9}$ A/mm

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C = 50 mg/l, en solution hydroalcoolique à 30° G.L. tamponnée à pH 9.3 par un mélange $NH_4Cl + NH_4OH$. Cette courbe, reproductible quant à sa forme, ne se prête pas à des mesures.

Dans les mêmes conditions, mais à pH 9.7, on obtiendra des polarogrammes tels que celui de la Fig. 2 (C = 100 mg/l), avec deux vagues de réduction bien dessinées.

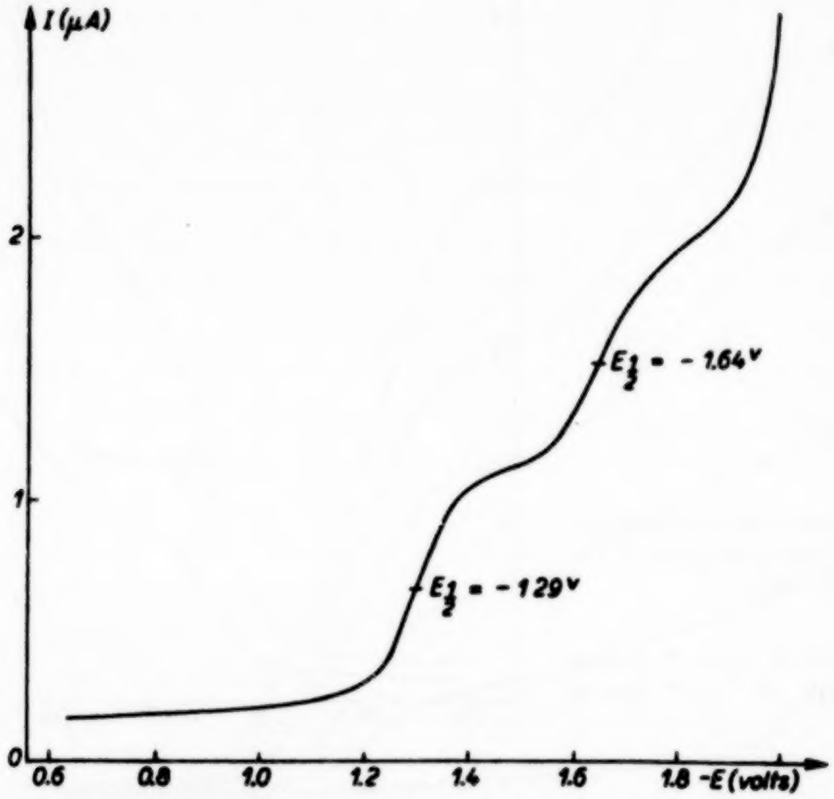

Fig. 2. Polarogramme de la phényl-2 oxine en milieu hydroalcoolique (50° G.L.), pH = 9.7. Sensibilité: 10^{-8} A/mm

Ces deux vagues, dont les hauteurs sont du même ordre, sont comparables à celles observées avec l'oxine par STONE ET FURMAN[4] dans des conditions peu différentes; mais elles sont situées à des potentiels moins négatifs:

$E_{\frac{1}{2}}$ = —1.29 et —1.64 V pour la phényl-2 oxine
$E_{\frac{1}{2}}$ = —1.39 et —1.76 V pour l'oxine[4], à pH 10.

D'un point de vue plus quantitatif il est cependant apparu que les courants de diffusion I_d de la première vague pour différentes concentrations C ne satisfaisaient pas, ou mal, à la loi d'ILKOVIC. C'est ainsi que pour des concentrations comprises entre 20 et 200 mg/l, le rapport I_d/C a pris des valeurs diverses entre 2.41 et 3.06 μA/m.mole/l.

Ces écarts pouvant être dus à des variations de concentration ou de pH, malgré les précautions prises pour éviter l'entraînement des produits volatils, il nous a paru préférable de travailler en milieu aqueux.

Milieu aqueux

Seuls, les pH extrêmes permettent alors d'avoir en solution une quantité de phényl-2 oxine suffisante.

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1. *En milieu très acide,* à pH 1.1 (tampon HCl—KCl), on observe une vague (Fig. 3), peu nette parce qu'immédiatement suivie de la décharge des ions de l'électrolyte support. On observe l'habituelle diminution de la surtension de l'hydrogène que produisent les dérivés de la quinoléine.

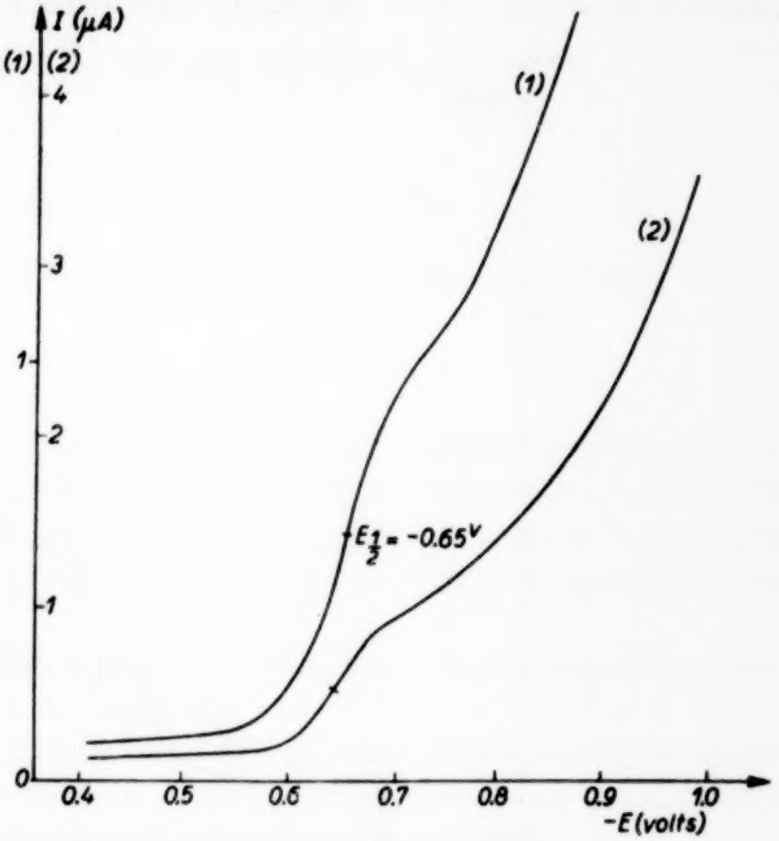

Fig. 3. Polarogrammes de la phényl-2 oxine en milieu aqueux acide, pH = 1.10. Concentration: 200 mg/l.

Courbe 1. Sensibilité $6.3 \cdot 10^{-9}$ A/mm
Courbe 2. Sensibilité $16 \cdot 10^{-9}$ A/mm

2. *En milieu très alcalin,* à pH 12, et en présence de 0.01% de gélatine, les polarogrammes obtenus (Fig. 4) présentent deux vagues B et C dont la première, bien détachée, se prête aux mesures.

Les chiffres correspondant aux polarogrammes de la Fig. 4 sont rassemblés dans le Tableau I. Les conditions de travail sont les suivantes:

pH: 12. Tampon: borax 0.02*M* — NaOH 0.06*N*
Température: 20-21° C
Hauteur du mercure: 35.5 cm
Débit du mercure: 2.83 mg/s à —1.60 V
2.85 mg/s à —1.74 V
Durée de vie des gouttes: 2.54 sec à —1.60 V
2.45 sec à —1.74 V
$m^{2/3} \cdot t^{1/6} = 2.33$
Désaération par barbotage d'azote pur: 5 bulles par seconde pendant 20 minutes.

TABLEAU I

C *mg/l*	*C* *m.mole/l*	$-E_{\frac{1}{2}}$ *V*	I_d *μA*	I_d/C *μA/m.mole/l*
20	0.090	1.494	0.345	3.81
40	0.181	1.480	0.69	3.81
72	0.326	1.476	1.21	3.71
100	0.453	1.478	1.695	3.75
140	0.634	1.480	2.345	3.70
180	0.815	1.477	3.025	3.71

$E_{\frac{1}{2}}$: potentiel de demi-vague.
I_d: courant de diffusion corrigé (courant total moins courant résiduel).

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Un dosage est ainsi réalisé pour des concentrations de l'ordre de 10^{-3} à 10^{-4} mole/litre. En utilisant la sensibilité maximum de l'appareil ($1.6 \cdot 10^{-9}$ A/mm) nous avons pu mesurer jusqu'à 10^{-5} mole de phényl-2 oxine par litre.

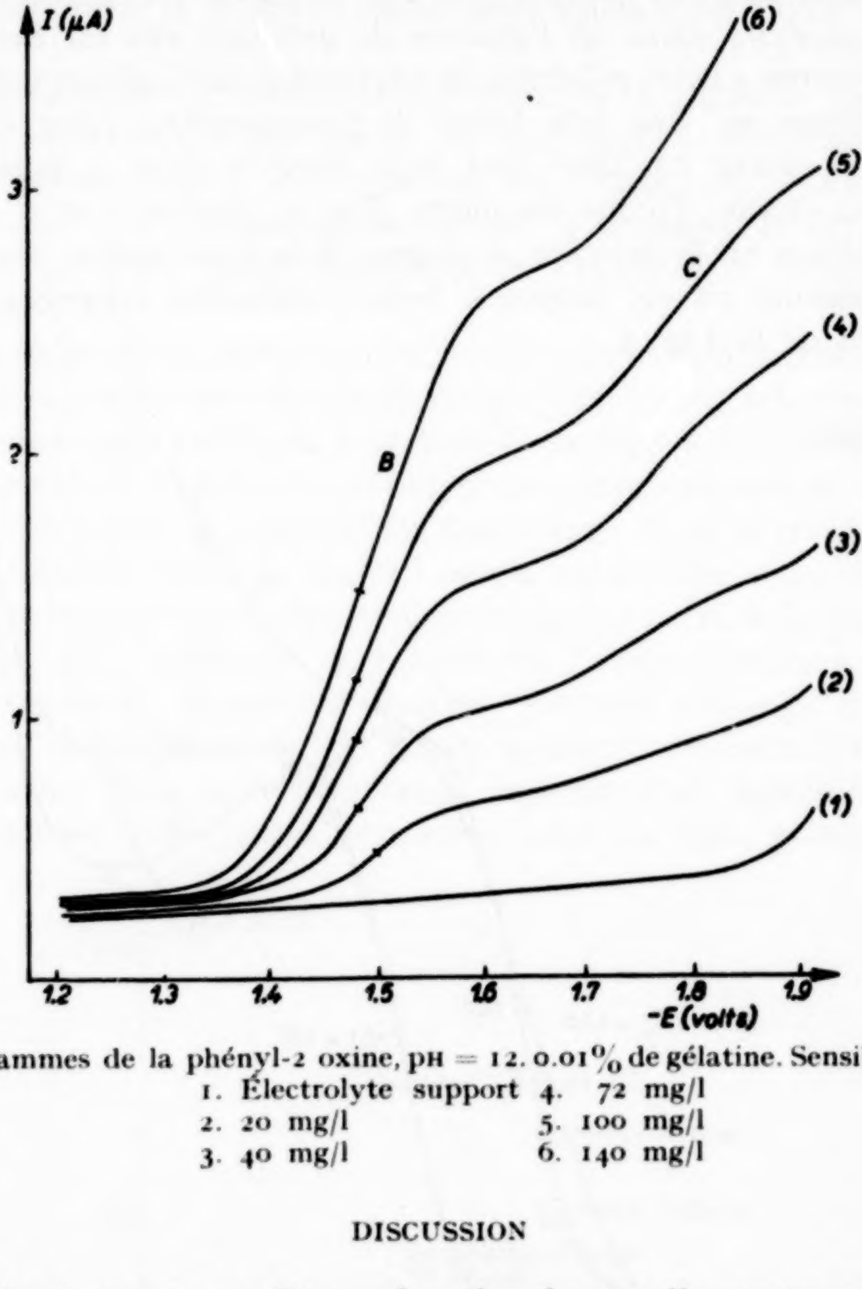
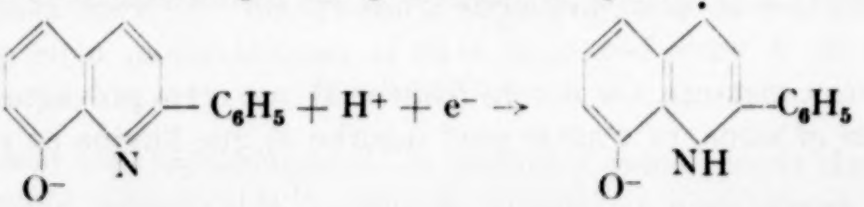


Fig. 4. Polarogrammes de la phényl-2 oxine, pH = 12. 0.01% de gélatine. Sensibilité: 10^{-8} A/mm.

1. Électrolyte support
2. 20 mg/l
3. 40 mg/l
4. 72 mg/l
5. 100 mg/l
6. 140 mg/l

DISCUSSION

Si notre étude n'est pas complète en fonction du pH, elle montre cependant que le comportement de la phényl-2 oxine est dans l'ensemble analogue à celui de l'oxine, tel qu'il a été décrit par STOCK[3]. En particulier, les résultats ci-dessus nous permettent de préciser que la réduction polarographique de la phényl-2 oxine à pH 12 met en jeu $n = 1$ électron; cette valeur, de n se déduit de l'équation classique d'ILKOVIC, en introduisant les valeurs de I_d/C et de $m^{2/3} \cdot t^{1/6}$ indiquées plus haut, et en prenant pour valeur approchée du coefficient de diffusion D le chiffre[3] de l'acide quinaldique, soit $D = 0.80 \cdot 10^{-5}$ cm^2·sec^{-1} à 25°C. On peut donc considérer comme plausible la formation d'un radical libre par un processus tel que:



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Ces conclusions concernent les courbes de la Fig. 4, obtenues *en présence de 0.01 % de gélatine:* si la raison de cette addition de gélatine n'a pas été précisée plus haut, c'est parce que ce point mérite d'être examiné de plus près, comme on s'en convaincra aisément en se reportant aux courbes 3 et 4 de la Fig. 5. La courbe 3 est le polarogramme de la phényl-2 oxine en l'absence de gélatine; elle est évidemment très différente de la courbe 4 (avec gélatine), en particulier par l'existence d'un maximum M et d'un minimum m. Une telle forme de polarogramme n'est sans doute pas exceptionnelle: SOUCHAY ET SER[5] l'ont déjà observée dans la polarographie des oximes en milieu alcalin; l'oxine elle-même (Fig. 5, courbes 1 et 2) présente dans les mêmes conditions un phénomène analogue. Mais il ne semble pas qu'une interprétation satisfaisante ait été proposée. Nous résumerons comme suit nos observations à propos de la Fig. 5.

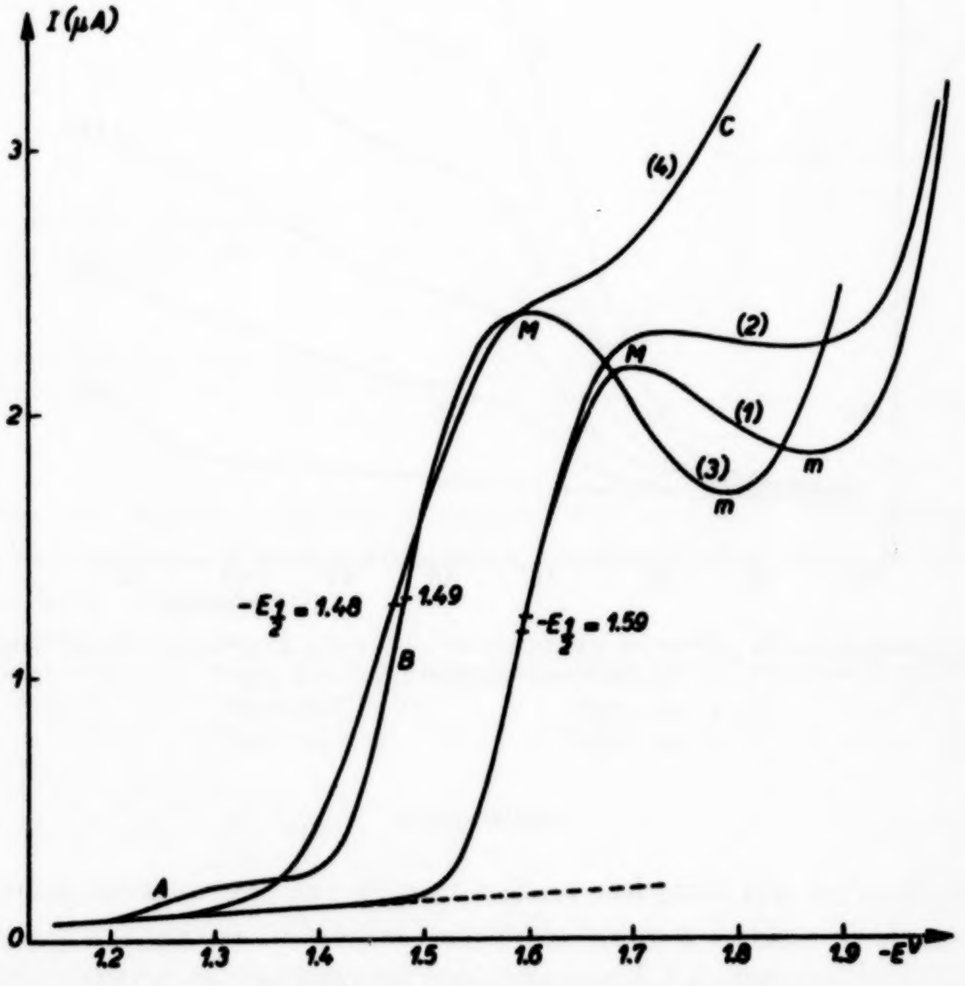

Fig. 5. Polarogrammes avec et sans gélatine, pH = 12.
1. Oxine 100 mg/l, sans gélatine.
2. Oxine 100 mg/l, avec gélatine.
3. Phényl-2 oxine 140 mg/l, sans gélatine.
4. Phényl-2 oxine 140 mg/l, avec gélatine.

1. Le polarogramme de la phényl-2 oxine sans gélatine (courbe 3) présente, outre la vague de réduction B, une „prévague d'adsorption" A. Nous avons pu observer que la position de A varie beaucoup avec la concentration, mais que sa hauteur semble à peu près constante. On notera (courbe 4) que cette prévague est supprimée par l'addition de gélatine, et d'autre part (courbe 1) que l'oxine ne présente pas ce phénomène.

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2. Le maximum M n'est pas un maximum semblable à ceux que l'on observe habituellement en polarographie: l'addition de gélatine ne le supprime pas, mais supprime le minimum m qui lui fait suite. Le courant en M est peu différent du courant de diffusion; pour la phényl-2 oxine nous avons vérifié qu'il suit bien la loi d'ILKOVIC.

3. La gélatine a aussi une action sur la pente de la vague B, dans le cas de la phényl-2 oxine seulement. Pour l'oxine on sait[3] que la réduction est réversible; appliqué aux courbes 1 ou 2, le critère de réversibilité de TOMES[6] nous donne $E_{1/4} - E_{3/4} = 0.061$ V. Ce même critère permet d'envisager la réversibilité de la réduction de la phényl-2 oxine seulement en l'absence de gélatine (courbe 3: $E_{1/4} - E_{3/4} = 0.060$ V).

4. On notera enfin que la phényl-2 oxine est réduite à des potentiels moins négatifs que l'oxine. Ceci est conforme à la règle de SHIKATA ET TACHI[7], selon laquelle l'électronégativité du substituant facilite la réduction. Cette règle a été vérifiée quantitativement par BROCKMAN ET PEARSON[8], qui ont trouvé, avec une série de benzophénones, une relation linéaire entre le potentiel de demi-vague $E_{\frac{1}{2}}$ et la constante de substitution σ de HAMMETT. Dans le cas des oxines substituées nous disposons d'une autre grandeur en liaison avec la densité électronique au point de la molécule intéressé par la réduction: pK_1, constante de basicité de l'atome d'azote quinoléique. Les valeurs de pK_1 et de $E_{\frac{1}{2}}$, de sources diverses, que nous avons pu rassembler dans la représentation graphique de la Fig. 6 sont nettement en accord avec la règle de SHIKATA ET TACHI. Mais seule une étude expérimentale systématique pourrait permettre de préciser une éventuelle relation entre ces deux grandeurs.

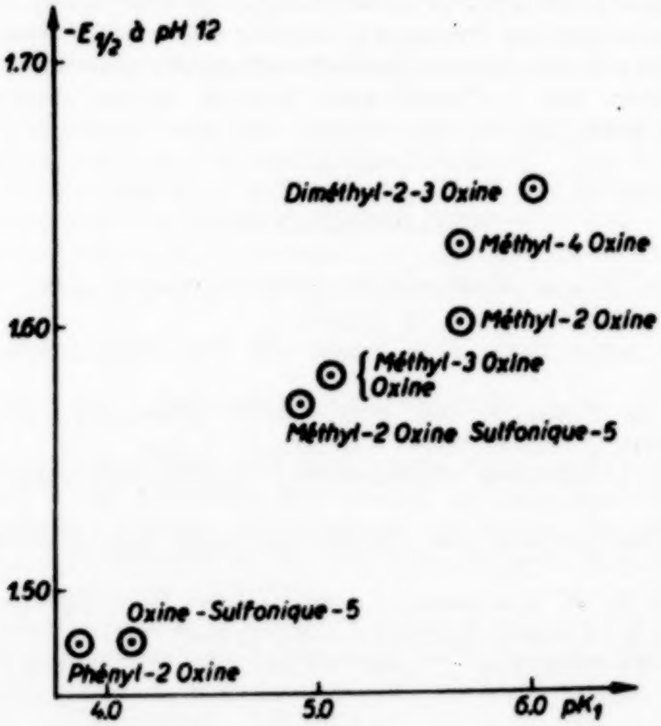

Fig. 6. Influence des substituants sur la réduction polarographique de l'oxine.

CONCLUSIONS

Le comportement polarographique de la phényl-2 oxine, décrit dans cet article, est, dans l'ensemble, comparable à celui de l'oxine, et nous avons indiqué dans

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quelles conditions il est possible d'envisager un dosage de ce réactif. Il est également intéressant de rapprocher nos résultats de ceux des études antérieures de composés de la même famille[3,9,10].

Nous insistons sur un point qui mériterait une étude plus approfondie: la forme inhabituelle des polarogrammes de la phényl-2 oxine à pH 12 (Fig. 5) — forme curieusement modifiée par la présence d'une faible quantité de gélatine au sein de la solution.

Enfin, nous avons vérifié que la diminution de la basicité de l'atome d'azote s'accompagne d'un accroissement de la facilité de réduction polarographique.

RÉSUMÉ

Les auteurs ont examiné polarographiquement la phényl-2 oxine. Par cette méthode le dosage s'est révélé possible, mais moins sensible que par spectrophotométrie (10^{-5} contre 10^{-6} mole/l). D'intéressantes observations ont pu être faites au cours de cette étude, en ce qui concerne le comportement polarographique de ce nouveau réactif, en particulier à pH 12.

SUMMARY

The authors have examined 2-phenyloxin polarographically. They have found that an estimation is feasible, but not as sensitive as with the spectrophotometer (10^{-5} instead of 10^{-6} mol/l). Some interesting observations have been made during this work, especially about the polarographic behaviour, at pH 12, of this new reagent.

ZUSAMMENFASSUNG

Die Verfasser haben das 2-Phenyloxin polarographisch untersucht. Hierbei hat sich herausgestellt, dass eine Bestimmung des Reagenzes mittels der polarographischen Methode möglich aber weniger empfindlich ist, als durch Spektrophotometrie (10^{-5} gegen 10^{-6} Mol/l). Über das polarographische Verhalten des 2-Phenyloxins wurden einige interessante Beobachtungen, insbesondere bei pH 12, gemacht.

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Reçu le 18 avril 1956

BOOK REVIEW

Advanced Analytical Chemistry by WALTER WAGNER, CLARENCE J. HULL AND GERALD E. MARKLE, Reinhold Publishing Corporation, New York, 1956, 282 pp. $ 6.—

This book is designed primarily for advanced students to introduce some of the newer developments, instrumental techniques, and modern theories of analytical chemistry. The word "Advanced" in the title must be interpreted strictly in the light of this fact. The book, which is divided into two sections, opens with a chapter on the more important organic reagents used in inorganic analysis. The classical methods of gas analysis are examined and the text then passes on to a very brief treatment of colorimetry and spectrophotometry, polarographic methods, chromatography and ion exchange, thermogravimetry, radiochemistry and statistics. Part II of the book deals with methods for the separation and determination of various elements. These are arranged according to their grouping in the periodic table. Under each element, various weighing forms and similar useful information are listed and a brief discussion is usually given of one method. Most surprisingly the method selected for discussion is frequently an inferior one, *e.g.* pride of place is given to the sulphate method for sodium. The authors do of course mention the triple acetate method but the student for whom the book is designed might well conclude that the sulphate method is the one generally used. No comparison is made with the triple acetate or any other method. The same somewhat surprising type of selection is made in the case of potassium. Sodium tetraphenylboron just receives a mention, yet this reagent has attained such wide usage in the last 5 years that already some half-dozen review articles on its applications have appeared. The one method described in detail is the rarely-used periodate method.

The authors have commendably avoided turning this book into a practical instruction manual. This has the advantage of allowing the book to be used with practically any make of instrument or apparatus, since no specific instructions on actual instrumental procedure are given.

The degree to which any particular technique or method is taught varies from institution to institution. The reviewer feels that the chapter on chromatography and ion exchange and that on radiochemistry might profitably be expanded somewhat, but of course this is a matter of individual taste. The general applicability and limitations of various techniques and methods should be more clearly emphasized, since the student needs more definite guidance at this stage in his training.

The ethylene bridge is omitted from the formula ascribed to EDTA on p. 19 and on page 129 the statement "magnesium may be determined with . . .; oxine as magnesium oxinate; 8-hydroxyquinoline as the respective complex" may lead the unwary beginner to attribute separate identities to oxine and 8-hydroxyquinoline.

The student will find this text to be a satisfactory introduction to the subjects discussed and many teachers will find useful points throughout the book.

R. BELCHER (Birmingham)

BUCHBESPRECHUNG

Handbuch der analytischen Chemie. Hrsg. von FRESENIUS UND JANDER. *II. Teil: Qualitative Nachweisverfahren. Band IV b, V/ab,* Elemente der vierten Nebengruppe und der fünften Gruppe. Titan - Zirkonium - Hafnium - Thorium - Stickstoff - Phosphor - Arsen - Antimon - Wismut - Vanadium - Niob - Tantal - Protactinium. Mit 105 Abbildungen. XV + 756 Seiten, Gr.-8°. 1956. Ladenpreis: DM 144.—, Ganzleinen DM 148.—

II. Teil: Qualitative Nachweisverfahren. Band IX: Vorproben und Trennungen der Kationen und Anionen. Analyse durch Vorproben. Lösen und Aufschließen. Trennungsgänge. Bearbeitet von A. IEVENS, K. STEGEMANN, M. E. STRAUMANIS. Mit 20 Abbildungen. XV + 311 Seiten, Gr.-8°. 1956. Ladenpreis: DM 63,—, Ganzleinen: DM 67.—

In beiden Bänden werden sehr viele Methoden erschöpfend behandelt. Durch einen äusserst klaren und übersichtlichen Aufbau wird das Studium dieser Werke wie auch das schnelle Nachschlagen sehr erleichtert. Neben den klassischen Nachweisverfahren findet man eine sorgfältige Auswahl der modernen Methoden. Den Nachweisverfahren auf mikroskopischem, biologischem und chromatographischem Wege sowie der Polarographie wird die gebührende Aufmerksamkeit geschenkt. Durch diese reichliche Auswahl sowie durch die vielfältigen Angaben für den Nachweis in besonderen Fällen wird das Werk das Interesse weitester Kreise finden.

W. RÜEDI (Genf)

BOOK REVIEW

Ionenaustauscher im Laboratorium und in der Industrie, Swiss Chemical Association, Zürich, 1955, 60 pages, 60 figures.

This short publication contains the substance of four lectures delivered at the symposium on "The chemistry and uses of ion-exchange in science and technology", arranged by the Swiss Chemical Association at Lausanne in October, 1954. With the exception of the third part, which is in French, the four articles are in German although the first two have summaries in French.

Part I, by Prof. H. DEUEL AND K. HUTSCHNEKER, describes natural materials which have ion exchange properties, the preparation of synthetic ion-exchange resins of all kinds and gives a simple description of the many factors which affect the distribution of ions between resin and solution in the batch process.

Part II, by Prof. W. BUSER AND DRS. P. GRAF AND W. F. GRÜTTER, is concerned with the general physical chemistry of ion-exchangers. Titration curves and the kinetics of exchange are interpreted, the validity and limitations of the application of the law of mass action and the Donnan equilibrium to the ion-exchange process are explained, and the section ends with a short description of column and membrane theory.

Part III, by Dr. G. BRUNISHOLZ describes the applications of ion-exchange in analytical and preparative chemistry. Practical details of column construction and operation for the laboratory are given.

Part IV, by Drs. H. HOEK AND E. SAILER, is concerned with the applications of ion exchange in industry (both by batch process and by the use of columns or membranes). At least half this section deals with the demineralization of water. It is unfortunate that the data released at the Geneva Conference on Atomic Energy on the purification of uranium by anion exchange were not available at the time of publication to redress what would nowadays be a lack of balance in this aspect of the subject.

In all, this monograph gives a comprehensive review of its subject. The authors have wisely concentrated on covering the whole field in general, and have not allowed themselves to be diverted by individual facets of the subject *e.g.*, the mathematical treatment of the column process is not described in detail but references which allow a detailed examination are given in full. Two further features are especially worthy of appreciation. The diagrams are numerous and apposite and a comprehensive list is given in Table 8 of the names and properties of some hundred different resins from various countries. The references are also complete up to the autumn of 1955 and comprise some 1300 in all. They are perhaps the most valuable feature of all.

There is something of interest to all who use ion-exchange resins in this small book, since it is obvious that great pains have been taken to make it compact, comprehensive, and as up-to-date as possible. For the research worker in particular, it is a useful source-book of information.

M. J. CABELL (Harwell)

REMARKS ON THE ANALYSIS OF PEROXY COMPOUNDS AND ON THE NATURE OF THE INDUCTION REACTIONS INVOLVED

by

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The literature on the chemistry of peroxy compounds often contains contradictory data resulting mainly from the inaccuracies of the analytical procedures applied. Therefore, in order to study systems involving hydrogen peroxide and various peroxy-acid-forming acids, the development of suitable analytical methods has first been attempted.

The RIESENFELD-LIEBHAFSKY[1] test, as is known, reveals whether the compound examined is a "true" one or a loosely bound addition peroxy compound. The test is rather delicate and, according to a number of authors, does not settle the question in a satisfactory way. Therefore, the WILLSTÄTTER[2] test was also used here, to control the RIESENFELD-LIEBHAFSKY test. On shaking the solid sample of perhydrates (hydrogen peroxides of crystallization) in an organic solvent, hydrogen peroxide splits off from the loosely bound addition peroxy compounds. Hydrogen peroxide can be detected in the usual way in the solution filtered of solid substances. The so-called "true" peroxy compounds undergo no change of this kind.

The "true" peroxy compounds fall, according to their structure, into two categories: (1) Compounds containing an -O:O-group, namely peroxides, and (2) compounds containing an -OOH group, hydroperoxides. This classification may also be justified on the basis of chemical properties, since the reactivity of the peroxide compounds of symmetrical structure is always less than that of the unsymmetrical hydroperoxides. These two groups are readily distinguished if the weakly acidic solution of the compounds to be examined is reacted with bromide or arsenite ions. Hydroperoxides of high reactivity oxidize the bromide or arsenite ions rapidly, while peroxides form bromine or arsenate, but very slowly. However, in the presence of suitable catalysts, such as osmic acid, or ions yielding compounds with the -OOH group (*e.g.* molybdate, wolframate, vanadate ions) the reaction does proceed. Peroxides which hydrolyse very slowly are unable, even in the presence of a catalyst, to oxidize the ions mentioned. Such compounds are the acyl peroxides or peroxy di-acids. Thus, the tests being carried out in the proper order, the presence of the following types can be established:

(a) hydroperoxides (compounds oxidizing the bromide and arsenite ions rapidly),

(b) peroxides (compounds reacting with the above-mentioned ions, but in the presence of catalysts),

(c) acyl peroxides or peroxy di-acids (compounds not undergoing any reaction with the above-mentioned ions, even in the presence of a catalyst).

Besides hydrogen peroxide, the so-called metal peroxides, (acidic and normal salts of hydrogen peroxide), organic peroxides and the compounds containing co-ordinated hydrogen peroxide behave as peroxides.

The compounds of R-OOH type behave as hydroperoxides where R=alkyl, aryl, acyl radicals.

It must be emphasized, however, that the above tests are applicable only to aqueous solutions.

Our method for the determination of compounds of these different types was developed on the basis of a detailed examination of the H_2O_2-H_2SO_5-$H_2S_2O_8$ system. The previous methods of analysis of the system can be arranged into classes according to the method of measurement of the hydrogen peroxide and peroxy acid content.

(1) Selective oxidation of hydrogen peroxide with the aid of $KMnO_4$ or $Ce(SO_4)_2$,

(2) Application of a KI reduction to the determination of hydrogen peroxide and peroxy acids,

(3) Selective decomposition of H_2O_2 with the aid of a catalyst.

The methods based on the selective oxidation involve certain experimental errors. The reduction procedures, since potassium iodide is a not sufficiently selective reagent, are rather cumbersome. The catalytic decomposition can be applied only to solutions containing hydrogen peroxide and stable peroxy di-acids, for compounds of a hydroperoxide type will be decomposed by the catalyst. Since the greatest potentialities seemed to be offered by the selective oxidation procedure, detailed investigations have been carried out in order to elucidate the causes of errors already observed by other authors. For the purpose of simplifying the examinations, the errors appearing in the permanganometric and cerimetric titrations of hydrogen peroxide-peroxydisulphuric acid system and that of hydrogen peroxide-peroxysulphuric acid system have been studied separately.

In carrying out the titration of hydrogen peroxide either with potassium permanganate or with cerium(IV)-sulphate it has been shown that not only the quantity of hydrogen peroxide but also that of peroxydisulphate is incorrect. The ratio of the H_2O_2 error to the $H_2S_2O_8$ was about 1. The same ratio was found on titrating hydrogen peroxide in the presence of peroxysulphuric acid. Therefore, the error was considered to be due to a reaction of a mole ratio 1:1 involving hydrogen peroxide and peroxy acid.

In order to decide whether or not the assumption of the above reactions is reasonable, the reactions between H_2O_2 and $H_2S_2O_8$ and between H_2O_2 and H_2SO_5, respectively, have been examined. It has been established that these reactions proceed slowly and result in the decomposition of hydrogen peroxide and peroxy acids with formation of O_2. The rate of reaction is largely dependent upon the hydrogen ion concentration of the solution. The rate of reaction increases with the increase of the pH. Accordingly, the H_2O_2 error observed shows a very strong dependence on the pH. The value of the error increases considerably with decreasing acid concentration. The value of the error also varies with the varying amounts of H_2O_2 or peroxy acids. The value of the error rises on increasing the concentration of either the H_2O_2 or the peroxy acids, while keeping, at the same time, the quantity of the other component constant. Thus the reaction between H_2O_2 and the peroxy acids may be reasonably regarded as leading to error. However, our examinations show that the above reactions are slow ($t_{1/2}$ = *ca.* 2—6 days in the case of 0.1*M* solution, depending on the acid concentration). Therefore, they would not lead to error if their rates would not be increased by the reactions H_2O_2-$KMnO_4$ and H_2O_2-$Ce(SO_4)_2$, respectively. In other words, the reactions are of induction character.

The induction character of the reactions is proved by the fact that the magnitude of the error, *i.e.* that of the induced reaction, is primarily dependent on the course and the rate of the inducing (or primary) reaction:

Inducing or primary reactions:

$$5\,H_2O_2 + 2\,KMnO_4 + 3\,H_2SO_4 \rightarrow K_2SO_4 + 2\,MnSO_4 + 5\,O_2 + 8\,H_2O$$
$$H_2O_2 + 2\,Ce(SO_4)_2 \rightarrow Ce_2(SO_4)_3 + O_2 + H_2SO_4$$

Induced reactions:

$$H_2O_2 + H_2S_2O_8 \rightarrow 2\,H_2SO_4 + O_2$$
$$H_2O_2 + H_2SO_5 \rightarrow H_2SO_4 + O_2 + H_2O$$

If the titration is carried out slowly, *e.g.* if the titrant is added in drops, the error increases. On the other hand, if greater amounts of titrant were used, the error again increased.

The interesting observation that the error increases when the volume of the solutions to be titrated is increased points to the same fact. If the same amounts of H_2O_2 and of peroxy acid are diluted to different extents, but at the same time care is taken to maintain the constancy of the pH of the solution, the error increases considerably. Under proper conditions the rate of the inducing reaction was measured and because of the dilution was found to be greatly decreased. The observed induction error, *i.e.* the extent of the induced reaction, is proportional to the rate of the inducing (or primary) reaction.

The decrease of the rate of the inducing reaction increases the induced change, probably because the rate of reaction running between the intermediates formed in the inducing (or primary) reaction and the titrant decreases on dilution and, therefore, for the induction reaction partner (here peroxy acid) a higher intermediate concentration is available. In order to examine the errors due to dilution, measurements are in progress.

The investigations have been extended to the examination of the neutral salt effect observable in the induction reaction. Our investigations carried out so far show that the neutral salts contribute considerably to the decrease in the induction error, which may be caused by the increase in the rate of the inducing reactions. It is probable that the role of the high manganese(II) sulphate concentration, which, it was pointed out by a number of authors, causes a decrease in the induction error, is different from that previously interpreted. It was formerly considered to undergo in the presence of manganous salt a so-called Guyard reaction, forming manganese dioxide, the reaction of which with hydrogen peroxide no longer results in an induction error. In our view, manganese(II) sulphate considerably accelerates the reaction between H_2O_2 and $KMnO_4$, as a result of which the error decreases. The same can be observed in the cerimetric measurements if greater amounts of cerium(III) ions are added to the solution.

It can be shown that the induction error increases considerably with increasing temperature. Naturally also the rate of the inducing (primary) reaction may increase with increasing temperature, whereby the extent of the induced change decreases. If the rise of the temperature results in the increase of the induction error, it is merely due to the fact that the rate of the induced reaction depends on the temperature to a greater extent than that of the inducing reaction.

The kinetic character of the induction error is supported by the fact that the induced reaction can be catalysed. Cupric ions exert such a catalytic effect that they are able to increase the induction error 10- to 15-fold.

On the basis of the observations made in the titration of a solution containing hydrogen peroxide and peroxydisulphuric acid with permanganate, it should be pointed out that the conclusions of some authors are erroneous, *e.g.* it has been observed that the induced reaction between hydrogen peroxide and peroxydisulphuric acid sets in without the presence of manganese(II) ions, contrary to FRIEND'S[3] findings. The observation that the error appearing in the system in question is caused by the induction reaction between permanganate and peroxydisulphuric acid, as stated by SKRABAL AND VACEK[4], cannot be accepted in view of our measurements. The findings of RIUS AND ZULUETA[5] that the induction error increases in the presence of larger quantities of manganese(II) sulphate must similarly be rejected. This behaviour could be observed only if the manganous sulphate preparation applied contained trace impurities of ferric and cupric ions. As pointed out above, the cupric ions are able, in small amounts, to give rise to the induction error by the catalysis of the induced reaction.

The effects observed in the above systems are evident in the permanganometric and cerimetric titration of a solution containing hydrogen peroxide and peroxysulphuric acid. As a slight quantitative deviation from the H_2O_2-$H_2S_2O_8$ system it may be noted that in the presence of peroxysulphuric acid the induction error is greater. Another effect could be observed, namely if the substances in question are titrated with potassium permanganate rapidly, or a large amount of titrant is added without stirring, the ratio of the H_2O_2 error and of the H_2SO_5 error is much smaller than 1. This is due to the effect of the titrant, which is temporarily in excess, resulting in the decomposition reaction between $KMnO_4$ and H_2SO_5 observed by other authors, during the course of which oxygen, and to a smaller extent ozone, is formed. A greater decomposition can be observed if the titration is carried out with ceric sulphate instead of permanganate. The decomposition reaction is largely dependent on the acid concentration of the solution, the quality of the acid applied (not pH but anion effect) and on different neutral salts. Our measurements, carried out in order to elucidate the decomposition observed, will be described in the near future.

The elucidation of the main characteristics of the induction effect rendered it possible to elaborate a method of sufficient accuracy for the simultaneous determination of H_2O_2, peroxysulphuric and peroxydisulphuric acid. The procedure was as follows. The most reactive compound, peroxysulphuric acid, was reduced by arsenious acid and then the H_2O_2 present measured with the aid of ceric sulphate. The measurement could be carried out, on the one hand because the ceric ions undergo a reaction with arsenious acid only in the presence of a catalyst, and on the other because the induction error taking place in the reaction between H_2O_2 and peroxydisulphuric acid is inhibited by arsenious acid. The arsenious acid takes over the role of H_2O_2, and thus the induction reaction will be that of the arsenious and peroxydisulphuric acid. Therefore, on applying an osmic acid catalyst in another sample, the amounts of H_2O_2 and of peroxysulphuric acid were simultaneously determined. Then peroxydisulphuric acid was measured in the same sample with another portion of arsenious acid. The measurement proved to have been rapid and exact and according to the observations the ions possibly appearing in this system did not interfere with the determination.

The determination can be carried out directly with arsenious acid as titrant by the following procedure.

Peroxysulphuric acid is titrated first, adding potassium bromide to the solution, then H_2O_2 is measured, applying an osmic acid catalyst, and finally peroxydisulphuric acid is titrated while heating. The end-point is indicated by the dead stop or the bimetallic systems. In the dead stop titrations the bromide-bromine redox system can be applied as depolarisator.

According to our examinations, both the indirect cerimetric and the direct arsenious acid methods are not only suitable for the analysis of the system H_2O_2-H_2SO_4 but may also be applied in all cases where compounds of peroxide, hydroperoxide or peroxy di-acids are measured (*cf.* the above-mentioned classification). Thus, for example, the method has been applied to the determination of H_2O_2 and peroxyacetic acid, and of H_2O_2 and peroxyphosphoric acids in the same solution, where induction reactions similar to the above take place.

An extensive account of these experiments will be published in the *Acta Chimica Hungarica* under the title: "Beiträge zur Analyse der Peroxy-Verbindungen".

SUMMARY

Simple reactions have been described for distinguishing between peroxy compounds of different types. The possibilities for analysis in the H_2O_2-H_2SO_4 system have been submitted to careful study and in this connection the main characteristics of the induction reactions involved have been elucidated.

RÉSUMÉ

Des réactions simples sont décrites pour distinguer entre eux divers types de composés peroxy. Les possibilités d'analyse dans le système H_2O_2-H_2SO_4 ont été étudiées attentivement et les principales caractéristiques des réactions d'induction qui ont lieu ont été expliquées.

ZUSAMMENFASSUNG

Es wurden einige einfache Reaktionen beschrieben, die eine Unterscheidung zwischen verschiedenen Typen von Peroxy-Verbindungen ermöglichen. Die Analysemöglichkeiten in dem System H_2O_2-H_2SO_4 wurden eingehend untersucht; in diesem Zusammenhang wurden die wichtigsten Charakteristiken der in dem System induzierten Reaktionen aufgeklärt.

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THE SENSITIVITY TO METAL IONS OF SOME CARBOXYLIC ACIDS DERIVED FROM PYRIDINE OR QUINOLINE

by

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HOLMES, REED AND CRIMMIN[1] have shown that the sensitivity of the reaction between anthranilic acid and metal ions is usually decreased by the buffer present, generally an acetate buffer. It has been recorded by FLAGG[2] that the cupric complex of quinoline-8-carboxylic acid is more soluble in acetic acid than in sulphuric acid of the same pH. In view of this it was thought desirable to study the effect of acetate buffers on the sensitivity of precipitations using quinoline-8-carboxylic acid and other similar heterocyclic acids.

Several divalent metal ions were used with quinoline-8-carboxylic, quinoline-2-carboxylic, picolinic, 6-methylpicolinic and *iso*quinoline-1-carboxylic acids, and the sensitivities of the reactions were found as described previously for anthranilic acid by HOLMES *et al.* The buffers were the same as those used on that occasion.

The pL values obtained are given in Table I; once more only upper limits have been quoted.

TABLE I

Acid	*Metal ion*	*Buffer*			
		A	*B*	*C*	*U*
Quinoline-8-carboxylic	Cu^{+2}	4·8	4·1	4·9	5·1
Quinoline-2-carboxylic	Cu^{+2}	4·8	4·8	4·8	4·8
	Ni^{+2}	N.P.	N.P.	N.P.	N.P.
	Co^{+2}	N.P.	N.P.	N.P.	N.P.
	Cd^{+2}	3·3	3·3	3·3	3·3
	Zn^{+2}	4·3	4·3	4·3	4·3
*iso*Quinoline-1-carboxylic	Cu^{+2}	5·2	5·2	5·2	5·2
	Ni^{+2}	3·9	3·9	3·9	3·9
	Co^{+2}	4·9	4·9	4·9	4·9
	Zn^{+2}	4·1	4·1	4·1	4·1

With quinoline-8-carboxylic acid no precipitate was formed with any of the common divalent cations except copper, nor with trivalent iron, aluminium or chromium.

Under the conditions of the test neither picolinic acid nor 6-methylpicolinic acid

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gave a precipitate with any of the common divalent or trivalent cations, even when these were present in concentration much greater than 1 mg per ml.

*iso*Quinoline-1-carboxylic acid is clearly the most generally efficient precipitant but its lack of selectivity, like that of quinoline-2-carboxylic acid, makes it a not very useful analytical reagent. With neither of these acids are the metal derivatives soluble in acetate buffers; the copper salt of quinoline-8-carboxylic acid is appreciably soluble, however, as reported by WELCHER.

The stability constants of the complexes considered here have been determined by HOLMES AND CRIMMIN[3,4]. The overall constant for copper quinoline-8-carboxylate is greater than that for the quinaldinate. Thus the explanation tentatively put forward for the solubility of metal anthranilates in acetate buffers cannot hold here. Further work is proceeding on this problem.

SUMMARY

The sensitivities of the reactions between metal ions and heterocyclic acids similar to picolinic acid have been determined. Only the complex formed by cupric ions with quinoline-8-carboxylic acid is found to be less soluble in unbuffered than in acetate buffered solutions.

RÉSUMÉ

La sensibilité des réactions, entre des ions métalliques et les acides hétérocycliques du type de l'acide picolinique, a été déterminée. Seul le complexe du cuivre (II) avec l'acide quinoléine-8-carboxylique est moins soluble dans des solutions non tamponnées que dans des solutions tamponnées à l'acétate, contrairement aux autres complexes.

ZUSAMMENFASSUNG

Die Empfindlichkeit der Reaktionen zwischen Metallionen und heterozyklischen Säuren vom Typus der Pikolinsäure wurde bestimmt. Nur die Komplexverbindung zwischen Kupfer(II)-Ionen und Chinolin-8-carbonsäure erwies sich als weniger löslich in ungepufferten als in mit Acetat gepufferten Lösungen.

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THE DETERMINATION OF ZINC IN WOOD PRESERVING SOLUTIONS

by

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The ferrocyanide titration of zinc has recently been studied by RICHARDSON AND BRYSON[1] and in conjunction with *o*-dianisidine as the indicator provides a satisfactory means of estimating this metal. In wood preservatives of the chromated zinc chloride and zinc-chrome-arsenate and copper-zinc-chrome-arsenate types chromate and copper interfere. The reduction of the chromate to trivalent chromium causes an interference due to the colour of the chromium masking the colour of the indicator. However, if the amounts of chrome are about equal to the concentration of zinc, zinc can be titrated, but better results are obtained if the chromium content is reduced. Thus in any procedure where zinc is to be estimated interference from these metals must be overcome and the following method was developed to solve this problem and has been found to give excellent results.

METHOD

Outline

Chromium is removed by extraction with methyl *iso*-butyl ketone in 1:1 hydrochloric acid, copper is then precipitated with cupferron and the zinc titrated in the filtrate.

Reagents

Hydrochloric acid, concentrated
Hydrochloric acid, 1:1
Methyl *iso*-butyl ketone (commercial)
Sulphuric acid, concentrated
Nitric acid, concentrated
Ammonia, 1:1
Acetic acid (glacial)
Cupferron, 2% in distilled water
Urea
Potassium ferrocyanide, 21 g/litre standardized against a standard zinc solution
Potassium ferricyanide, 0.5%
o-Dianisidine, 0.1%. 0.1 g of the indicator is dissolved in 1 ml of conc. H_2SO_4 and diluted to 100 ml with distilled water. The solution deteriorates on keeping and should be made fresh each month.

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Procedure

(a) Separation of the chromium

Place the sample containing about 10-20 mg of zinc in 10 ml of solution in a 125 ml separating funnel. Add 10 ml of conc. HCl and 20 ml of methyl *iso*-butyl ketone, shake and allow the layers to separate. Collect the lower aqueous layer in a 150 ml beaker and wash the ketone layer with two 5 ml portions of 1:1 HCl collecting these in the beaker. Since the Cr^{+6} is readily reduced in strong HCl this operation should be completed with the least possible delay.

To the aqueous extracts add 1 ml of conc. H_2SO_4 and 10 ml conc. HNO_3, cover and take to fumes of SO_3.

(b) Separation of the copper

(1) To the contents of the beaker add 30 ml of distilled water and ammonia dropwise to the appearance of a precipitate. Re-dissolve the precipitate with glacial acetic acid and add 20 drops in excess. Cool to room temperature.
(2) Add 3 ml of cupferron solution with stirring, allow the precipitate to settle and filter through a Whatman No. 4 filter washing the precipitate twice with cold water.
(3) Collect the filtrate and washings in a 150 ml beaker, add 1.5 ml of conc. H_2SO_4 and 10 ml of conc. HNO_3, cover and take to fumes of SO_3.

(c) Titration of the zinc

(1) Set up a 5 ml microburette and fill to the zero with standard ferrocyanide.
(2) Add 30 ml of distilled water to the contents of the beaker, heat to boiling and add 0.5 g of urea to remove oxides of nitrogen.
(3) Add a few drops of the standard ferrocyanide from the burette. Then four drops of indicator and 1-2 drops of ferricyanide. The solution now becomes the deep reddish-brown of the oxidized colour of the indicator.
(4) Continue the titration with measured amounts of ferrocyanide until the colour changes permanently to the greenish-white of the reduced form of the indicator. Because of the slowness of the precipitation of zinc ferrocyanide, after each addition of reagent the indicator temporarily changes to the reduced form and this is especially so near the end-point. RICHARDSON AND BRYSON refer to a peculiar false end-point phenomenon and this is also observable in the titration with the indicator. The solution assumes a reddish-violet colour and then fades to the reduced colour when 80-90% of the required ferrocyanide has been added. The reddish-brown colour is restored after vigorous stirring and then the titration can be continued.
(5) Standardize the ferrocyanide against a known zinc solution.

RESULTS

Results obtained by the method are shown in Table I where they are compared with analyses by a procedure involving removal of the copper by thioacetamide and precipitation of the zinc as oxinate followed by a titration using the bromate-bromide procedure. As can be seen the results agree well with the alternative procedure.

TABLE I

Sample	*Oxine method*	*Zn g/litre* *New method*	*Difference*
Zinc-chrome-arsenate	2.92	2.93	+ 0.01
	2.59	2.57	— 0.02
	0.63	0.63	0.00
Copper-zinc-chrome-arsenate	0.31	0.33	+ 0.02
	0.65	0.62	— 0.03
	0.80	0.81	+ 0.01
	1.21	1.22	+ 0.01
	1.56	1.59	+ 0.03

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NOTE ON THE USE OF METHYL *iso*-BUTYL KETONE

The use of methyl *iso*-butyl ketone in the above method is an outcome of an investigation into methods of determination of trace elements in rocks, which the author was making when John Edmond Fellow at the University of Otago, New Zealand. It was necessary to remove the iron sufficiently completely to permit the determination of this metal in the extract.

Procedures for extracting iron using oxine, bromoxine, 1-nitroso-2-naphthol, salicylaldehyde and acetoacetic ester with and without masking agents were tried without achieving a really satisfactory separation. A further survey of the literature revealed the work of KUZNETSOV[2] on the distribution of ferric chloride between hydrochloric acid solutions and organic solvents. Methyl *iso*-butyl ketone appeared the most promising of these substances and was further studied. The distribution coefficient of iron between the reagent and 1:1 HCl was found to be 2,500 for $0.1M$ Fe^{+3} and this value remained fairly constant over the range 5-$7N$ HCl. It was therefore possible to extract the iron completely from the aqueous phase and subsequently return the iron to the aqueous phase by washing with distilled water. The determination was quantitative. Chromate was found to have a distribution coefficient of 50, Cu^{+2} 0.1, vanadate was also extracted though to a less extent than chromate. Alkali and alkaline earth metals, cobalt, nickel, zinc, aluminium, titanium and trivalent chromium were not extracted. It was also found that by treatment of a mixture of the above components with hydrogen peroxide, then making 1:1 in hydrochloric acid only iron and a trace of copper were extracted, since hydrogen peroxide masks vanadate against extraction and chromate is converted to the trivalent chromium through decomposition of the perchromate. This reagent is believed to be superior to any of the current methods in use for the extraction of iron from aqueous solution.

ACKNOWLEDGEMENTS

The method described was developed and used in the Dominion Laboratory, Auckland, New Zealand. The comparison between the method and that used by the Analytical Division, Boliden Mining Company, Skelleftehamn, Sweden, was made by the author while a guest of the Research Department of the Boliden Company. The author is indebted to Mr. K. M. GRIFFIN, Government Analyst, Auckland, New Zealand for his interest in the work and to the Boliden Company for the opportunity to carry out the comparative analyses.

SUMMARY

A method is described for determining zinc in wood-preserving solutions by titration with ferrocyanide. Copper and chromate interfere and are removed. A note is appended on the use of methyl *iso*-butyl ketone in analysis.

RÉSUMÉ

L'auteur décrit une méthode de dosage du zinc, dans des solutions de préservation du bois, par titrage au moyen du ferrocyanure. Le cuivre et l'anion chromique gênent et doivent être éliminés. L'article est complété par une note sur l'utilisation de la méthyl-*iso*-butyl-cétone en analyse.

ZUSAMMENFASSUNG

Eine Methode zur Bestimmung von Zink in Holzimprägnierungslösungen durch Titration mit Ferrocyanid wird beschrieben. Kupfer und Chromat stören und müssen deshalb entfernt werden. Es folgt eine kurze Mitteilung über die Verwendung von Methyl-*iso*-butyl-keton in der Analyse.

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5:6-BENZOQUINALDINIC ACID AS AN ANALYTICAL REAGENT

III. DETERMINATION OF MERCURY

by

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In a recent paper[1] reference to the use of the reagent 5:6-benzoquinaldinic acid for the estimation of mercury has been made. This paper provides the procedure for the determination of mercury, the pH regions of its complete precipitation and the method of its separation from other elements.

From a study of the pyrolysis curves of the mercury complexes with the organic reagents, DUVAL[2] recommended the adoption of the methods based on precipitation as dipyridinomercury bichromate[3], bis-(propylene-diamino)-copper iodomercurate[4], bis-(biguanido)-copper iodomercurate[5], and thionalide[6].

Of the methods, the first requires precipitation in a neutral medium and a complicated wash liquid, the second, though applicable only in the neutral or faintly ammoniacal medium, is ineffective in presence of copper, cobalt, zinc, chromium and ammonium salts.

The method based on biguanide requires strictly controlled conditions and even then for satisfactory results the mercury solution should be free from other ions except those of halogens and be kept overnight.

The dipyridine complex has a very short range of stability and requires complicated wash liquids.

The thionalide method requires conversion of mercuric nitrate to chloride and a three-fold excess of the reagent for complete precipitation.

Recently SEDIVEC[7] utilized Bismuthiol II for the gravimetric estimation of mercury at a high pH in presence of Complexone III, without which the precipitates showed to have variable composition. This method gives quite satisfactory results in presence of a number of elements.

5:6-Benzoquinaldinic acid, the subject of this paper, effects the complete precipitation of mercury at pH 1.9 to 6.0 and its separation from ammonium salts, salts of alkalis, alkaline earths, rare earths, magnesium, chromium, iron, aluminium, thorium, titanium, zirconium, uranium (UO_2^{+2}), lead, bismuth, sulphate, nitrate, molybdate, vanadate, tungstate, arsenate and phosphate.

The mercury complex is anhydrous at 100°C and stable up to 150°C and is insoluble in dilute acids and in organic solvents.

EXPERIMENTAL

Reagents and apparatus

Chemicals used were all of reagent quality. Standard solutions were prepared from reagents of highest purity and their strengths were determined by the standard procedures. Rare earth solution, free from thorium, was prepared in the same way as referred to in the previous communication[1]. A solution of mercuric nitrate with a little nitric acid, to prevent hydrolysis, was used as the standard solution whose mercury content was determined by both the SEDIVEC[7] and VOLHARD[8] methods.

As precipitant, a 1% solution of the sodium salt of 5:6-benzoquinaldinic acid of m.p. 187°C (1 g of 5:6-benzoquinaldinic acid in 100 ml water) was used.

pH measurements were made with a bench model pH meter.

Composition of the mercury complex

The mercury salt of the reagent was precipitated from a hot nitrate solution, containing tartrate to prevent hydrolysis, by the slow addition of the reagent and the precipitate after filtration and washing was dried at 110°C. A weighed amount of the complex, thus prepared, was decomposed by digestion with perchloric acid and the mercury content was determined by the VOLHARD method. The complex was thus found to have the composition $Hg(C_{14}H_8O_2N)_2$ [% Hg calc. 31.12; found 31.15, 31.08].

Study of the pH range

An aliquot portion of the mercuric nitrate solution was taken in a beaker with about 1 g of tartaric acid and diluted to 300 ml. This was neutralized with ammonia to the yellow colour of methyl red indicator and acidified with dilute nitric or acetic acid to adjust the pH at different level. The solution was heated nearly to boiling and a slight excess of the reagent solution was added dropwise with stirring till the mercury completely precipitated. The precipitate was then filtered, washed with hot water, dried at 110°C and weighed. The pH of precipitation was determined from the filtrate (see Table I).

TABLE I

Hg taken *mg*	$Hg[C_{14}H_8O_2N]_2$ *mg*	*Hg found* *mg*	*pH*
9.865	31.3	9.741	1.7
9.865	31.8	9.896	1.9
15.4	49.6	15.43	2.7
15.4	49.5	15.40	3.2
23.1	74.2	23.09	4.0
23.1	74.1	23.06	5.9
23.1	74.1	23.06	6.1
23.1	73.8	22.97	6.5

Separation of mercury from diverse ions

A solution of mercury (23.1 mg of Hg) and the ion from which it was to be separated were taken in a beaker. 2.5 g of tartaric acid and about 2 g of ammonium nitrate were added to the solution which was diluted to 300 ml. The precipitate that appeared was dissolved by dilute nitric acid and the solution was neutralized with ammonia to the yellow colour of methyl red indicator. It was then acidified with dilute nitric or acetic acid and followed the procedure referred to above (see Table II). For the separation of mercury from lead, 1 g of ammonium acetate was added to the solution acidified with acetic acid before the addition of the reagent. Chromium remained in solution in presence of tartrate only when the solution was warmed before neutralization.

TABLE II

Ions added *mg*		*$Hg[C_{14}H_8O_2N]_2$* *mg*	*Hg found* *mg*
Mg^{+2}	100	74.3	23.12
Ca^{+2}	100	74.2	23.09
Sr^{+2}	100	74.0	23.03
Ba^{+2}	100	74.1	23.06
Fe^{+3}	100	74.2	23.09
Al^{+3}	100	74.3	23.12
R_2O_3	100	74.2	23.09
Cr^{+3}	50	74.2	23.09
Th^{+4}	100	74.1	23.06
Ti^{+4}	50	74.0	23.03
Zr^{+4}	50	74.4	23.15
UO_2^{+2}	50	74.5	23.18
Pb^{+2}	50	74.4	23.15
Pb^{+2}	75	74.5	23.18
Bi^{+3}	50	74.3	23.12
Bi^{+3}	100	74.4	23.15
MoO_4^{-2}	166.7	74.2	23.09
VO_4^{-3}	225.5	74.0	23.03
WO_4^{-2}	134.7	74.3	23.12
PO_4^{-3}	153.5		
AsO_4^{-3}	92.7	74.1	23.06

SUMMARY

5:6-Benzoquinaldinic acid has been utilized for the estimation of mercury in the presence of ammonium salts, salts of alkali, alkaline earths, rare earths, magnesium, chromium, iron, aluminium, thorium, titanium, zirconium, uranium (UO_2^{+2}), lead, bismuth, sulphate, nitrate, molybdate, vanadate, tungstate, arsenate and phosphate.

RÉSUMÉ

L'acide 5,6-benzoquinaldinique a été utilisé pour le dosage du mercure en présence de sels d'ammonium, sels alcalins et alcalino-terreux, sels de terres rares, magnésium, chrome, fer, aluminium, thorium, titane, zirconium, uranium (UO_2^{+2}), plomb, bismuth, et des ions sulfuriques, nitriques, molybdiques, vanadiques, tungstiques, arséniques et phosphoriques.

ZUSAMMENFASSUNG

Die 5.6-Benzochinaldinsäure wurde zur Bestimmung von Quecksilber in Gegenwart der folgenden Substanzen angewendet: Ammonium-, Alkali- und Erdalkalisalze, Salze der seltenen Erden und von Magnesium, Chrom, Eisen, Aluminium, Thorium, Titan, Zirkonium, Uran (UO_2^{+2}), Blei und Wismuth, Sulphate, Nitrate, Molybdate, Vanadate, Wolframate, Arsenate und Phosphate.

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THE APPLICATION OF THIOSALTS IN ANALYSIS

II. ESTIMATIONS BASED ON DECOMPOSITION OF THIOSALTS PART D. ESTIMATION OF SELENIUM AND TELLURIUM IN SELENATES AND TELLURATES

by

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In a previous paper[1] from this laboratory it has been shown that selenium and tellurium can be estimated as sulphides by converting the selenite and tellurite into the corresponding thiosalts and subsequently decomposing the latter by the addition of an excess of dilute hydrochloric acid. It was pointed out that the method was not applicable to selenates and tellurates.

Further investigations have shown that if the thiosalts are formed by the addition of a large excess of the alkali sulphide, and then decomposed by the addition of a sufficient excess of concentrated hydrochloric acid, the precipitates of the sulphides are obtained in a granular form, are easily filtered and washed and after suitable treatment can be weighed directly as sulphides for the estimation of the metals. In case the quantities of alkali sulphide or hydrochloric acid are insufficient, the results obtained are too low.

EXPERIMENTAL

Estimation of selenium in selenates

A solution of potassium selenate was prepared and the exact quantity of selenium present in it was determined by first reducing the selenate to selenite with concentrated hydrochloric acid, and then precipitating the metal by means of sulphurous acid[2] or hydroxylamine hydrochloride[3,4].

Measured volumes of the standard potassium selenate solution were treated with a large excess of $2N$ sodium sulphide reagent[5] (prepared below 5°C) and the thiosalt formed was decomposed with a sufficient quantity of concentrated hydrochloric acid. It was found that if the amount of acid used to decompose the thiosalt is insufficient, the thiosalt is not decomposed completely. The concentration of the hydrochloric acid in the resulting mixture should be slightly above $6N$. The mixture was heated to boiling and then allowed to cool to the room temperature. During this operation the yellow precipitate first produced changed its colour to orange and became more easily filterable. The precipitate was filtered through a sintered glass crucible (porosity 4) washed free from chloride with distilled water, dried in an air oven at 95°C for an hour and weighed. It is not possible to dry the precipitate at 100°C as it begins to soften at this temperature and decomposes at a slightly higher temperature. The ratio:

$$\frac{\text{weight of the metal}}{\text{weight of the precipitated sulphide}} \text{ is } 0.4889.$$

The weights of metallic selenium contained in the measured portions of the solutions and those corresponding with the precipitate actually obtained are given in Table I.

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TABLE I

DETERMINATION OF SELENIUM IN SELENATES WITH $2N$ SODIUM SULPHIDE REAGENT

No.	Vol. of Se solution ml	Vol. of $2N$ Na_2S added ml	Vol. of $12N$ HCl added ml	Wt. of ppt. sulphide g	Wt. of Se in the ppt. g	Wt. of Se actually present g
1	25	50	85	0.0949	0.04640	0.04640
	28	60	100	0.1062	0.05192	0.05198
	30	70	110	0.1140	0.05573	0.05565
	33	50	90	0.1252	0.06120	0.06125
2	20	45	80	0.0760	0.03715	0.03712
	10	30	50	0.0379	0.01852	0.01856
3	25	55	90	0.1734	0.08476	0.08500
	20	45	75	0.1387	0.06782	0.06800
	10	30	45	0.0694	0.03393	0.03400

Estimation of tellurium in tellurates

For estimating tellurium in the hexavalent state a solution of potassium tellurate was prepared and standardized by first reducing the tellurate to tellurite by repeated treatments with concentrated hydrochloric acid, and then to metal with sulphurous acid and hydrazine hydrochloride[6]. It was observed that the direct reduction of tellurate with sulphurous acid and hydrazine hydrochloride as generally recommended gives too low results owing to incomplete reduction.

Measured volumes of the standard tellurate solution were treated with a large excess of $2N$ sodium sulphide reagent[5] and the thiosalt thus formed was decomposed with a sufficient excess of concentrated hydrochloric acid. The concentration of the acid in the resulting mixture was adjusted at a little above $6N$. The mixture was heated to boiling and allowed to cool to room temperature. During this operation the brown precipitate first produced, changed its colour to shining black.

The precipitate was filtered through a weighed sintered glass crucible (porosity 4) washed free from chloride ions with distilled water, dried in an air oven at 105°C for an hour and weighed. The ratio of Te:S in the precipitate is 1:3 corresponding with the formula TeS_3.

It is not possible to dry the precipitate above 106°C as it decomposes at a slightly higher temperature. On washing the precipitate of tellurium sulphide with alcohol and ether there is a progressive decrease in weight. This is probably due to the decomposition of the sulphide into the metal and sulphur and the dissolution of the sulphur thus formed in the solvent.

The weights of the metallic tellurium contained in the measured portions of the solutions and those corresponding with the precipitate actually obtained are given in Table II.

TABLE II

DETERMINATION OF TELLURIUM IN TELLURATES WITH $2N$ SODIUM SULPHIDE REAGENT

No.	Vol. of Te solution ml	Vol. of $2N$ Na_2S added ml	Vol. of $12N$ HCl added ml	Wt. of ppt. sulphide g	Wt. of Te in the ppt. g	Wt. of Te actually present g
1	25	60	95	0.2446	0.1395	0.1391
	20	55	85	0.1951	0.1113	0.1113
	10	40	60	0.0975	0.05560	0.05565
	5	30	45	0.0489	0.02789	0.02783
2	25	55	90	0.1228	0.07001	0.07000
	20	40	70	0.0981	0.05595	0.05601
	10	25	45	0.0492	0.02806	0.02800
3	25	45	80	0.0828	0.04722	0.04730
	25	35	70	0.0829	0.04729	0.04730

A note on the estimation of mercury

In an earlier publication[7] a method for the quantitative estimation of mercury based on the decomposition of its thiosalt with hydrochloric acid was proposed. Further investigation has shown that any ammonium salt can be used to decompose the thiosalt of mercury but for quantitative work treatment in the cold with ammonium acetate gives the best results as shown in the following Table III.

TABLE III

DETERMINATION OF MERCURY BY DECOMPOSING THE THIOSALT WITH AMMONIUM ACETATE, WASHING WITH WATER AND DRYING AT 105°C

No.	*Vol. of Hg solution ml*	*Vol. of 2N Na_2S added ml*	*Wt. of ppt. HgS g*	*Wt. of Hg in the ppt g*	*Wt. of Hg actually present g*
1	25	35	0.2165	0.1866	0.1867
	25	40	0.2165	0.1866	
	25	45	0.2166	0.1867	
2	20	30	0.1732	0.1493	0.1494
	20	40	0.1733	0.1494	
	20	45	0.1732	0.1493	
3	10	15	0.0866	0.07466	0.07470
	10	20	0.0865	0.07457	
	10	25	0.0865	0.07457	

The precipitate can also be washed with water, alcohol and ether successively, dried in a vacuum desiccator for half an hour and weighed.

SUMMARY

1. It has been shown that selenium in the hexavalent state can be precipitated quantitatively by adding an excess of the alkali sulphide reagent and then decomposing the thiosalt with a large excess of concentrated hydrochloric acid.
2. The quantity of the metal in the precipitate can be determined by multiplying the weight of the precipitate by a constant factor.
3. The same method is also applicable to the gravimetric estimation of tellurium when present in the hexavalent state. The ratio of Te:S in the precipitate obtained is 1:3.
4. It has been shown that ammonium acetate can be substituted for hydrochloric acid in the decomposition of the thiosalt when estimating mercury as mercuric sulphide.

RÉSUMÉ

1. Le sélénium(VI) peut être précipité quantitativement par addition d'un sulfure alcalin, en excès, et ensuite par décomposition du thiosel formé, au moyen d'un grand excès d'acide chlorhydrique concentré.
2. La teneur du métal dans le précipité peut être déterminée en multipliant le poids du précipité par un facteur constant.
3. Cette méthode peut également être appliquée au dosage gravimétrique du tellure(VI). Le rapport Te:S dans le précipité obtenu est de 1:3.
4. On peut remplacer l'acide chlorhydrique par l'acétate d'ammonium pour la décomposition du thiosel lors du dosage du mercure comme sulfure mercurique.

ZUSAMMENFASSUNG

1. Es wurde gezeigt dass sechswertiges Selen durch Zugabe eines Überschusses an Alkalisulfid und Zerstörung des gebildeten Thiosalzes mit überschüssiger konzentrierter Salzsäure vollständig gefällt werden kann.

2. Man erhält die in dem Niederschlag enthaltene Metallmenge indem man das Gewicht des Niederschlages mit einem konstanten Faktor multipliziert.
3. Die gleiche Methode kann zur gravimetrischen Bestimmung des sechswertigen Tellurs angewendet werden. Das Verhältnis von Te:S in dem Niederschlag ist 1:3.
4. Bei der Bestimmung von Quecksilber als Mercurisulfid kann das Thiosalz mit Ammoniumazetat statt mit Salzsäure zersetzt werden.

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SEPARATIONS INVOLVING SULPHIDES

I. SEPARATION OF SELENIUM, ARSENIC, ANTIMONY AND MERCURY FROM BARIUM

by

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In earlier publications[1,2] from this laboratory, methods for the estimation of various metals as sulphides have been proposed. Some of these methods are based on the formation and subsequent decomposition of thiosalts, while others involve the direct precipitation of sulphides by alkali sulphides. In all those estimations solutions of single substances were taken and so no separations were involved. But it is well known that various estimations which give perfectly correct results where single substances are involved, either fail completely or partially when the method is applied in the presence of other metals in the same solution. This is generally due to co-precipitation, but other complications may also take place.

With a view to study how far the methods proposed for the estimation of metals as sulphides are applicable in the presence of other metals in the same solution, a systematic investigation of their behaviour under these conditions is necessary. This will test the usefulness of the new methods in actual analysis, where we have to deal not with single substances but with mixtures. Such an investigation will also help us to determine the delicacy of the new scheme[3,4] of qualitative analysis based on the decomposition of thiosalts. For the special feature of this scheme is the separation of metals as sulphides under different conditions, and the efficacy of the scheme will thus depend upon the accuracy with which such separations can be carried out.

In view of what has been said above with regard to the objective of this series of investigation, it is proposed to divide the work under three heads:

(I) Separation of metals which form thiosalts from other metals like barium which are not precipitated as sulphides.

(II) Separation of metals which form thiosalts from others which form sulphides or hydroxides.

(III) Separation of metals forming sulphides from other metals which are not precipitated as sulphides.

This will cover all possible combinations of metals in which separations of sulphides are involved. This may appear an ambitious undertaking, but such an exhaustive investigation is necessary for testing and establishing the usefulness of the new methods proposed in the field of qualitative and quantitative analysis.

EXPERIMENTAL

In the following set of experiments the mixture containing the two metals is treated with an excess of the alkali sulphide reagent, the thiosalt formed with the metals of the arsenic group is decomposed with hydrochloric acid, the metals separated and estimated as sulphide, and barium in the filtrate estimated as usual in the form of $BaSO_4$.

(1) *Separation of selenium from barium*

A solution of selenious acid (AnalaR quality) was prepared and standardized by precipitating the metal with sulphurous acid[5], and also as sulphide[1]. Measured volumes of this solution were mixed with known volumes of a standard[6] barium chloride solution and the mixture was treated with 2*N* sodium sulphide reagent[7] in excess. The solution containing the thiosalt was acidified with a measured quantity of 2*N* hydrochloric acid, sufficient to produce a concentration of approximately 1*N* in the resulting mixture. The acid is to be added all at once. The mixture was heated till the yellow precipitate became orange in colour. After the precipitate had settled and cooled to room temperature, it was filtered through a weighed sintered glass crucible (porosity 4), washed thoroughly with distilled water, dried in an air oven at 95°C for one hour[8] and weighed.

The filtrate was boiled to expel hydrogen sulphide gas, and barium estimated as sulphate The results are given in Table No. I.

TABLE I

SEPARATION OF SELENIUM FROM BARIUM WITH 2*N* SODIUM SULPHIDE REAGENT

Vol. of Se solution ml	*Vol. of Ba solution* ml	*Vol. of the reagent added* ml	*Vol. of 2N HCl added* ml	*Wt. of Se in the ppt.* SeS_2 g	*Wt. of Se actually present* g	*Wt. of Ba in the ppt.* $BaSO_4$ g	*Wt. of Ba actually present* g
25	20	30	80	0.09326	0.09320	0.07709	0.07725
20	25	25	75	0.07461	0.07456	0.09661	0.09656
10	20	15	50	0.03730	0.03728	0.07709	0.07725
20	20	25	70	0.05584	0.05576	0.1406	0.1404
30	10	40	90	0.08368	0.08364	0.07012	0.0702
25.42	26.16	30	85	0.07102	0.07086	0.1771	0.1768

(2) *Separation of arsenic from barium*

A solution of sodium arsenate was prepared and standardized by precipitating it as sulphide[1], and also volumetrically[9] by conversion to silver arsenate and titrating as in Volhard's method. Measured volumes of this solution were mixed with known volumes of a standard[6] barium chloride solution and the mixture was treated with a large excess of 2*N* sodium sulphide reagent[7]. The solution containing the thiosalt was acidified with a measured quantity of concentrated hydrochloric acid sufficient to produce a concentration of approximately 6*N* in the resulting mixture. The mixture was heated to boiling, stirred and allowed to cool to the room temperature. The precipitate of As_2S_5 was filtered through a weighed sintered glass crucible (porosity 4), washed thoroughly with distilled water and alcohol, dried in an air oven at 100-110°C for an hour and weighed as As_2S_5.

In the filtrate, barium was estimated as sulphate.

The results are given in Table II.

TABLE II

SEPARATION OF ARSENIC FROM BARIUM WITH 2*N* SODIUM SULPHIDE REAGENT

Vol. of As solution ml	*Vol. of Ba solution ml*	*Vol. of the reagent added ml*	*Vol. of conc. HCl added ml*	*Wt. of As in the ppt.* As_2S_5 *g*	*Wt. of As actually present g*	*Wt. of Ba in the ppt.* $BaSO_4$ *g*	*Wt. of Ba actually present g*
25	25	35	95	0.06077	0.06075	0.09649	0.09656
25	10	25	70	0.06067	0.06075	0.03860	0.03862
20	25	30	85	0.04859	0.04860	0.10860	0.10875
20	20	25	75	0.04850	0.04860	0.08672	0.08700
35	20	40	110	0.08506	0.08505	0.1444	0.1442
25.22	26.13	50	120	0.06120	0.06130	0.1836	0.1835

(3) *Separation of antimony from barium*

A solution of antimony potassium tartrate (AnalaR quality) was prepared and standardized[1] by precipitating antimony as Sb_2S_3. Measured volumes of this solution were mixed with known volumes of a standard[6] barium chloride solution and the mixture was treated with a large excess of 2*N* sodium sulphide reagent[7]. The solution containing the thiosalt was acidified with dilute hydrochloric acid and heated to boiling. After the precipitate had settled, and cooled to room temperature it was filtered through a weighed sintered glass crucible (porosity 4) washed thoroughly with hot water, dried in an air oven at 105-110°C for an hour and weighed as Sb_2S_3.

In the filtrate barium was estimated as sulphate.

The results are given in Table III.

TABLE III

SEPARATION OF ANTIMONY FROM BARIUM WITH 2*N* SODIUM SULPHIDE REAGENT

Vol. of Sb solution ml	*Vol. of Ba solution ml*	*Vol. of the reagent added ml*	*Vol. of 2N HCl added ml*	*Wt. of Sb in the ppt.* Sb_2S_3 *g*	*Wt. of Sb actually present g*	*Wt. of Ba in the ppt.* $BaSO_4$ *g*	*Wt. of Ba actually present g*
25	25	75	120	0.1274	0.1273	0.1412	0.1412
25	10	80	125	0.1275	0.1273	0.05661	0.05649
10	25	35	75	0.05092	0.05092	0.1414	0.1412
25	20	75	120	0.1243	0.1242	0.1128	0.1130
21.30	26.40	75	120	0.1057	0.1058	0.1495	0.1491
26.40	21.30	80	125	0.1311	0.1311	0.1205	0.1203

(4) *Separation of mercury from barium*

A solution of mercuric chloride (AnalaR quality) was prepared and standardized[2] by precipitating it as sulphide. Measured volumes of this solution were mixed with known volumes of a standard barium chloride solution and the mixture was treated with a large excess of 2*N* sodium sulphide reagent to convert the mercury completely into its thiosalt. The mixture was acidified with dilute hydrochloric acid and heated to boiling. The precipitate of mercuric sulphide was allowed to settle, filtered through a weighed sintered glass crucible (porosity 4) and after suitable treatment weighed as HgS.

In the filtrate from mercuric sulphide, barium was estimated as sulphate.

The results are given in Table IV.

TABLE IV

SEPARATION OF MERCURY FROM BARIUM WITH 2*N* SODIUM SULPHIDE REAGENT

Vol. of Hg solution ml	*Vol. of Ba solution* ml	*Vol. of the reagent added* ml	*Vol. of 2N HCl added* ml	*Wt. of Hg in the ppt. HgS* g	*Wt. of Hg actually present* g	*Wt. of Ba in the ppt.* $BaSO_4$ g	*Wt. of Ba actually present* g
20	20	35	70	0.1190	0.1188	0.1080	0.1079
20	10	30	60	0.1188	0.1188	0.05391	0.05394
10	20	25	50	0.05948	0.05940	0.1080	0.1079
25	25	50	100	0.1862	0.1862	0.1351	0.1349
26.02	25.52	50	100	0.1929	0.1928	0.1444	0.1443
26.22	26.22	50	105	0.1945	0.1943	0.1480	0.1482

SUMMARY

It has been shown that the separations of selenium, arsenic, antimony and mercury from barium based on the decomposition of the thiosalts give sufficiently correct results in quantitative analysis.

RÉSUMÉ

Les séparations du sélénium, de l'arsenic, de l'antimoine et du mercure d'avec le baryum, basées sur la décomposition des thiosels donnent des résultats suffisamment précis pour l'analyse quantitative.

ZUSAMMENFASSUNG

Es wurde gezeigt, dass die Trennungen von Selen, Arsen, Antimon und Quecksilber vom Barium durch Zersetzung der Thiosalze für die quantitative Analyse genügend genau sind.

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LOW CONSTANT VAPOUR CONCENTRATIONS OBTAINED BY A DYNAMIC METHOD BASED ON DIFFUSION

by

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INTRODUCTION

In a number of investigations use is made of a gas flow containing low constant vapour concentrations. The following examples may be quoted:

a) the study of detection and quantitative estimation of impurities in air;
b) the measurement of adsorption from atmospheric air at low vapour concentrations;
c) testing the toxicity of compounds by inhalation;
d) the conditioning of air with low relative humidities.

Several methods have been used for this purpose, *e.g.*:

a) *Dilution* of a small quantity of saturated air, obtained by means of bubblers, with a large quantity of vapour-free air[1] at room temperature. In the case of liquids with relatively high vapour pressures extremely large quantities of pure air are needed for dilution to obtain the low concentrations desired. The accurate measurement of the necessary highly divergent rates of air flows together with the homogenization of the mixture are not easy to carry out. Another disadvantage of this method may be the decomposition of the liquid when large quantities of air have to be passed through it.
b) *Saturation* of air with vapour at low temperatures. In practice a difficulty turns out to be the cooling of the air to a constant low temperature. In a number of cases increases of the viscosity or solidification of the liquid to be vaporized occur.
c) *Vaporization* of drops of a solution containing the agent to be studied. A great disadvantage of this method lies in the fact that the air will contain not only the agent but also the vapour of the solvent which will in most cases invalidate the results.
d) *Diffusion* of the vapour through a porous wall into a gas flow[2]. By means of this method it is possible to obtain low and relatively constant concentrations at room temperature and without the use of a solvent. A disadvantage of this method is however the fact that the rate of diffusion is not reproducible and cannot be predicted.

The methods, mentioned above, which are commonly used or described in the literature, did not meet our requirements. We have however succeeded in developing a new method, which satisfies a general need in the laboratory and which is based on diffusion of the vapour through a cylindrical tube of known dimensions. In this way we are able to obtain reproducible low vapour concentrations at room temperature without the use of a solvent. In addition the values of the rate of diffusion and the vapour concentration can be predicted. By variation of the temperature of the diffusion unit, the dimensions of the tube and of the ratio of air and vapour to be mixed, a very wide range of vapour concentrations is obtainable.

THEORETICAL DISCUSSION

The diffusion of vapour in a tube has already been investigated by STEPHAN[3]. Other workers[4,5,6] have extensively used this method to determine the diffusion coefficient of many substances in the gaseous state. We have made use of the diffusion of vapours through a cylindrical tube in order to obtain a flow of air with constant and reproducible low vapour concentrations.

List of principal symbols used

Symbol	*Meaning*	*Dimension*
φ	diffusion flow (= the quantity of vapour diffused per unit of time)	mmol/sec
φ_m	maximum diffusion flow	mmol/sec
φ_0	unit flow	mmol/cm sec
Ø	the quantity of vapour diffused within a time t	mmol
A	cross sectional area of a tube	cm^2
l	length of a tube	cm
$\frac{A}{l}$	geometrical factor	cm
c_t	total concentration of gas mixture	mmol/ml
c	concentration of the vapour in the tube at a distance x from the entrance	mmol/ml
c_l	concentration of the vapour at the exit of the tube ($x = l$)	mmol/ml
c_0	concentration of the saturated vapour ($x = 0$)	mmol/ml
c_w	the low concentration wanted	mmol/ml
p_t	total pressure of a gas mixture	mm Hg
p	pressure of the vapour in the tube at a distance x from the entrance	mm Hg
p_0	saturated vapour pressure ($x = 0$)	mm Hg
p_l	vapour pressure at the exit of the tube ($x = l$)	mm Hg
D	diffusion coefficient	cm^2/sec
R	gas constant 62.36 8.31	ml mm Hg/°K mmol erg/°K mmol
T	absolute temperature	°K
v	rate of air flow through the diffusion unit	ml/min
v'	rate of flow of the vapour-free air	ml/min
λ	dilution factor defined as $\lambda = \frac{v}{v + v'}$	—
$\varkappa_\tau$	ratio of diffusion flows at τ°C and 20°C	—
M_1	molecular weight of the air	g/mol
M_2	molecular weight of the vapour	g/mol
V_1	molecular volume of the air	ml/mol
V_2	molecular volume of the vapour	ml/mol
a,b	constants of the equation $\log p_0 = a - b/T$	—
τ	temperature	°C
t	time	sec
x	variable distance from the entrance of the diffusion tube	cm
indices τ and 20	indicate the values of the properties considered at τ and 20°C respectively	—

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1. *Calculation of the quantity of vapour diffused*

The total mass of vapour, diffusing per unit of time through the cross section of a cylindrical vessel (see Fig. 1) may be calculated from[3]:

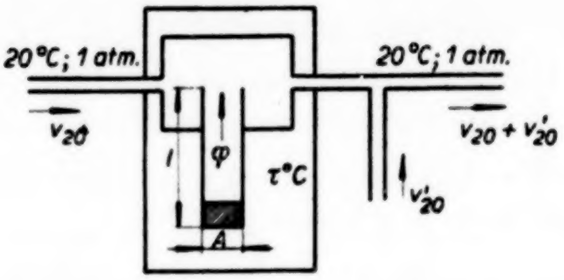

Fig. 1. A schematic reproduction of the diffusion unit used.

$$\varphi = \frac{\mathrm{d}\O}{\mathrm{d}t} = -AD \cdot \frac{c_t}{c_t - c} \cdot \frac{\mathrm{d}c}{\mathrm{d}x} \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$\text{As } p = c \cdot RT \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

we obtain from (1):

$$\varphi = -\frac{AD}{RT} \cdot \frac{p_t}{p_t - \mathrm{p}} \cdot \frac{\mathrm{d}p}{\mathrm{d}x} \quad \ldots\ldots\ldots\ldots \quad (3)$$

In the stationary state φ is constant and equation (3) may be integrated to:

$$\varphi = \frac{ADp_t}{lRT} \ln \frac{p_t - p_l}{p_t - p_0} \quad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

If $p_0 \ll p_t$ (*e.g.* $p_0 < 0.01\ p_t$), then the total mass of vapour leaving the vessel per unit of time may be calculated from:

$$\varphi = \frac{A}{l} \cdot \frac{D}{RT} (p_0 - p_l) \quad \ldots\ldots\ldots\ldots\ldots \quad (5)$$

At a rate of v ml/min of the air flow, the mass of vapour leaving the apparatus is then approximately:

$$\varphi = v\ c_l = \frac{v\ p_l}{RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

Hence combining the equations (5) and (6), we obtain:

$$\varphi = \frac{A}{l}\ \frac{Dp_0}{RT} \Big/ \left(1 + \frac{AD}{lv}\right) \quad \ldots\ldots\ldots\ldots \quad (7)$$

The maximum flow we define as the current:

$$\varphi_m = \frac{A}{l}\ \frac{Dp_0}{RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

It may be obtained from (7) by substituting $v = \infty$.

The unit flow φ_0 is obtained from equation (8) by substituting $\frac{A}{l} = 1$.

Hence:

$$\varphi_0 = \frac{Dp_0}{RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

2. *Influence of temperature*

At τ°C and 20°C we obtain respectively:

$$(\varphi_0)_\tau = \frac{D_\tau\,(p_0)_\tau}{RT_\tau} \tag{10}$$

and:

$$(\varphi_0)_{20} = \frac{D_{20}\,(p_0)_{20}}{RT_{20}} \tag{11}$$

The ratio $\varkappa_\tau$ of the unit flows at τ°C and 20°C is:

$$\varkappa_\tau = \frac{(\varphi_0)_\tau}{(\varphi_0)_{20}} = \frac{D_\tau \cdot T_{20} \cdot (p_0)_\tau}{D_{20} \cdot T_\tau \cdot (p_0)_{20}} \tag{12}$$

According to GILLILAND[6] the diffusion coefficient may be calculated from:

$$D = \frac{0.0043\,T^{3/2}\sqrt{\dfrac{1}{M_1}+\dfrac{1}{M_2}}}{p_t\,(V_1^{1/3}+V_2^{1/3})^2} \tag{13}$$

If p_t is expressed in atm, T in °K, M_1 and M_2 in g/mol, and V_1 and V_2 in ml/mol, the diffusion coefficient is obtained in cm²/sec.

The ratio of the diffusion coefficients may approximately be obtained from:

$$\frac{D_\tau}{D_{20}} = \left(\frac{T_\tau}{T_{20}}\right)^{3/2} \tag{14}$$

Generally the relation between the saturated vapour pressure p_0 and the absolute temperature T is given by:

$$\log p_0 = a - b/T \tag{15}$$

So the ratio of the saturated vapour pressures $(p_0)_\tau$ and $(p_0)_{20}$ is obtained from:

$$\log\frac{(p_0)_\tau}{(p_0)_{20}} = b\left(\frac{1}{T_{20}} - \frac{1}{T_\tau}\right) \tag{16}$$

Combining the equations (12), (14) and (16) the ratio $\varkappa_\tau$ of the unit flows may be calculated from:

$$\log\varkappa_\tau = b\left(\frac{1}{T_{20}} - \frac{1}{T_\tau}\right) + \frac{1}{2}\log\frac{T_\tau}{T_{20}} \tag{17}$$

3. *Adjustment of the quantity of diffusing vapour*

At τ°C we obtain from the equations (7), (10) and (12):

$$\varphi_\tau = \frac{A}{l}\cdot\varkappa_\tau\,(\varphi_0)_{20}\left(1+\frac{AD_\tau}{lv_\tau}\right)^{-1} \tag{18}$$

Hence the quantity of vapour, transported by diffusion is determined by three factors:

a) the *geometrical factor* $\frac{A}{l}$, which may be varied (between about 0.003 and 0.3 cm) by taking diffusion tubes of different dimensions;

b) the *physical factor* $\varkappa_\tau\ (\varphi_0)_{20}$ containing the temperature coefficient $\varkappa_\tau$ (between 20°C and 50°C we obtain about $1 < \varkappa_\tau < 10$) and the unit flow $(\varphi_0)_{20}$ at 20°C and 1 atm. The value of the unit flow $(\varphi_0)_{20}$ is dependent on the properties of the vapour, the diffusion medium (air) and on the total pressure (p_t) of the gas-mixture;

c) the *mixed factor* $\left(1+\frac{AD_\tau}{lv_\tau}\right)^{-1}$. Substituting relatively high values for $\frac{A}{l}$ and D_τ (respectively 0.4 cm and 0.1 cm²/sec) and a "normal" rate of air flow (100 ml/min) the mixed factor approximates the value of 1. This will also be the case for higher rates of air flow and for lower values of the geometrical factor $\frac{A}{l}$ and the diffusion coefficient D_τ. The "mixed factor" will therefore in general be near unity and have little influence on the diffusion flow.

4. *Adjustment of the vapour concentration.*

a) *General method* (see Fig. 1). A current of air (v_{20} ml/min at 20°C and 1 atm) is heated or cooled to a temperature of τ°C. To the air flow obtained ($v_\tau = v_{20} \cdot \frac{T_\tau}{T_{20}}$ ml/min at τ°C and 1 atm) a diffusion flow of vapour is added. If the vapour pressure is small in proportion to the total pressure of the gas mixture, the concentration may be obtained, combining the equations (2), (6) and (7), from:

$$(c_l)_\tau = \frac{(c_0)_\tau}{1+\frac{lv_\tau}{AD_\tau}} \quad \ldots\ldots\ldots\ldots\ldots \quad (19)$$

After cooling or heating the vapour containing air flow to a temperature of 20°C and mixing with v'_{20} ml/min air at 20°C and 1 atm, the concentration wanted may be obtained from:

$$\frac{c_w}{(c_0)_{20}} = \frac{\lambda \cdot \frac{(c_0)_\tau}{(c_0)_{20}} \cdot \frac{T_\tau}{T_{20}}}{1+\frac{lv_\tau}{AD_\tau}} \quad \ldots\ldots\ldots\ldots\ldots \quad (20)$$

where:

$$\lambda = \frac{v_{20}}{v_{20}+v'_{20}}$$

As

$$\frac{(c_0)_\tau \cdot T_\tau}{(c_0)_{20} \cdot T_{20}} = \frac{(p_0)_\tau}{(p_0)_{20}} \quad \ldots\ldots\ldots\ldots\ldots \quad (21)$$

the ratio of the concentration wanted and the concentration of the saturated vapour at 20°C is:

$$\frac{c_w}{(c_0)_{20}} = \frac{\lambda \cdot (p_0)_\tau/(p_0)_{20}}{1+\frac{lv_\tau}{AD_\tau}} \quad \ldots\ldots\ldots\ldots\ldots \quad (22)$$

b) *Limits of the applicability of the method.* When $\frac{lv_\tau}{AD_\tau} \gg 1$, which is generally the case (see above) we obtain from (22) by using the equation $v_\tau = v_{20}\frac{T_\tau}{T_{20}}$ and the relations (12) and (14):

$$\frac{c_w}{(c_0)_{20}} = \lambda\varkappa_\tau \frac{AD_{20}}{lv_{20}} \quad \ldots\ldots\ldots\ldots\ldots \quad (23)$$

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where $\lambda = 1$, if no extra air is added and $\varkappa_\tau = 1$, when the experiments are carried out at 20°C.

The saturation method, mentioned in the introduction, may be considered as an extreme case of the diffusion method in which $\frac{l}{A} = 0$ so that (22) changes to:

$$\frac{c_w}{(c_0)_{20}} = \lambda \frac{(p_0)_\tau}{(p_0)_{20}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (24)$$

In Table I a survey is given of the methods which we prefer in order to obtain relative concentrations of different values (see equation (22)). The rate of the air flow through the diffusion apparatus is in all 5 cases about 100 ml/min.

TABLE I

SUITABLE METHODS FOR DIFFERENT RANGES OF RELATIVE VAPOUR CONCENTRATIONS

Nr.	*Relative concentrations wanted*	*Variables*			*Constants*			*Methods*
	$\frac{c_w}{(c_0)_{20}}$	λ	τ	$\frac{A}{l}$	λ	τ	$\frac{A}{l}$	
1	1-0.05	1-0.05				20°C	∞	saturation and dilution
2	0.05-0.01		20°C-50°C		1		≈ 0.3	diffusion at higher temperatures
3	10^{-2}-10^{-4}			0.3-$0.3 \cdot 10^{-2}$	1	20°C		diffusion at 20°C
4	10^{-4}-$5 \cdot 10^{-6}$	1-0.05				20°C	$\approx 0.3 \cdot 10^{-2}$	diffusion and dilution
5	$< 5 \cdot 10^{-6}$		< 20°C		≈ 0.05		$\approx 0.3 \cdot 10^{-2}$	diffusion at lower temperatures and dilution

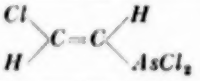
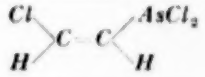
5. *Calculation of unit flows and temperature coefficients*

The unit flows $(\varphi_0)_{20}$ of some substances at 20°C and 1 atm in air have been calculated from diffusion coefficients obtained with equation (13) and saturated vapour pressures taken from the literature[9,10,11].

In Table II several data have been given. The molecular volumes have been determined from the atomic volumes of the composing elements[8]. In the case of hydrochloric acid the molecular volume has been taken from the literature[7]. In the

TABLE II

CALCULATED UNIT FLOWS $(\varphi_0)_{20}$ AT 20°C AND 1 atm

Substance	*Hydrochloric acid (36 . 36% in water)*	*Propionic acid*	*Lewisite I*		*Mustard gas*
			trans	*cis*	
Formula	HCl	C_2H_5COOH	 	 	$(ClCH_2CH_2)_2S$
M g/mol	36.44	74.1	207.3	207.3	159.1
V ml/mol	30.8⁷)	86.0	132.3	132.3	157.6
D cm²/sec	0.139	0.084	0.064	0.064	0.060
p_0 mm Hg	119⁹)	2.95⁹)	0.267¹¹)	1.13¹¹)	0.070¹⁰)
a	—	9.8757	—	8.4131	9.4819
b	—	2464.6	—	2450.2	3117.2
$(\varphi_0)_{20}$ $\frac{\text{mmol}}{\text{cm sec}}$	$98.3 \cdot 10^{-5}$	$1.35 \cdot 10^{-5}$	$0.093 \cdot 10^{-5}$	$0.394 \cdot 10^{-5}$	$0.023 \cdot 10^{-5}$
$(\varphi_0)_{20}$ $\frac{\mu g}{\text{cm min}}$	2150	60	11.6	49.0	2.2

last horizontal series where the unit flows at 20°C and 1 atm are given, one sees that their values vary roughly from 2 to 2000 μg/cm min. In Fig. 2 we have plotted the maximum diffusion flows against the geometrical factor $\frac{A}{l}$. The slopes of the lines are equal to the values of the unit flows mentioned above. The graph enables one to chose the necessary value of the geometrical factor for any desired value of the maximum diffusion flow. The values of the temperature coefficients of some substances have been calculated from equation (17) and are plotted against temperature in Fig. 3. The constants b have been taken from the literature[9,10,11]. The divergence between the curves is caused mainly by the difference in heat of evaporation between the substances considered. With the help of Figs. 2 and 3 and equation (18) we may determine the conditions required (dimensions of the diffusion tube and temperature) in order to obtain any value of the diffusion flow which may be desired.

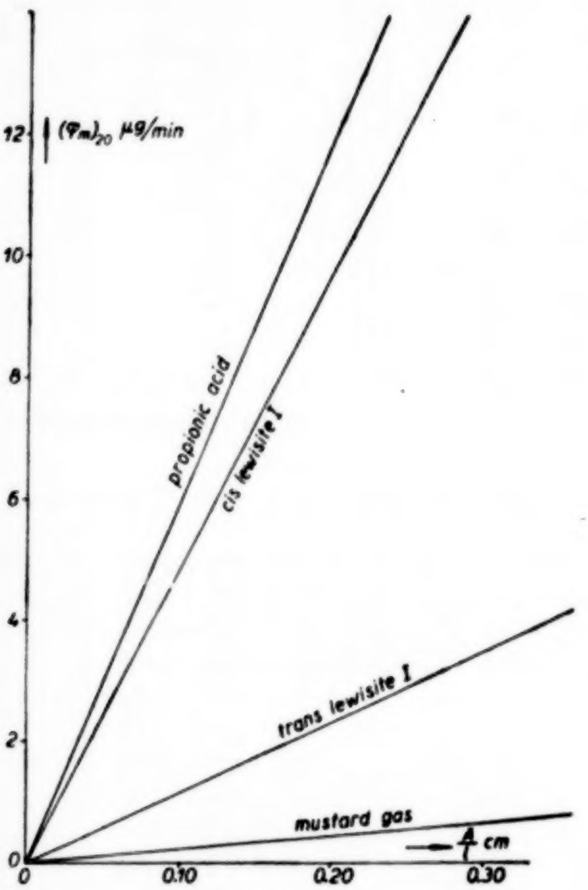


Fig. 2. The calculated diffusion flows of some substances as a function of the geometrical factor.

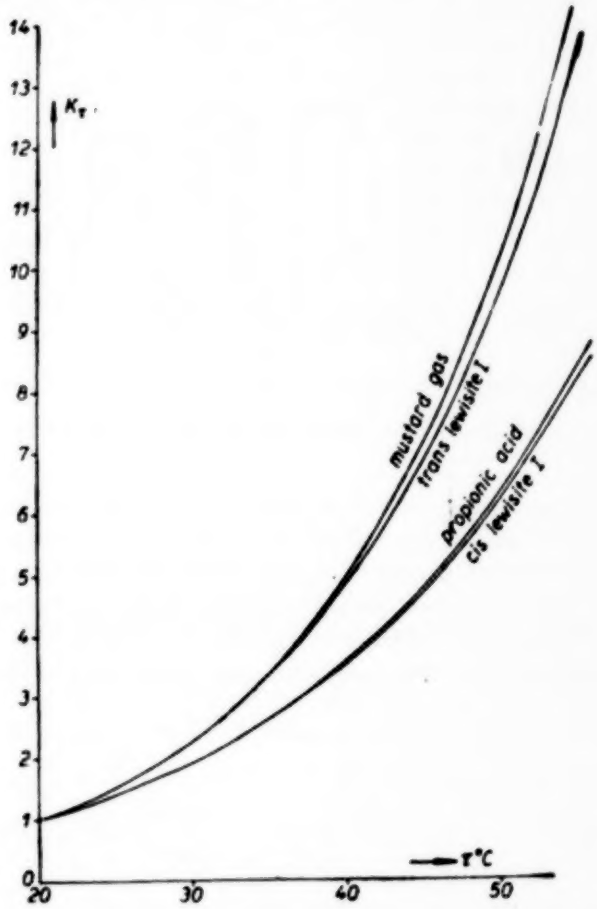


Fig. 3. The calculated ratio $\varkappa_\tau$ of the unit flows at τ°C and 20°C as a function of the temperature τ.

APPARATUS

1. *General*

Fig. 4a. gives a flow diagram of the apparatus. A current of air is passed via a buffer vessel B and two absorption towers A_1 and A_2 (absorbing water and carbon dioxide from the air respectively) through a rotameter preceded and followed by the cocks K_1 and K_2 respectively. In the mixer M of the vapour dosing apparatus the vapour is added to the air. Then the vapour containing air is passed into one of two absorption vessels F_1 and F_2 via a cock K_3. By turning the cock K_3 90° the vapour containing air will pass the other absorption vessel and the pressure in the mixer will be the same as before. The vapour concentration in the air was determined by analysing the contents of the absorption vessels. The quantity of vapour, diffused per unit of time, is only constant if pressure, temperature and rate of air flow remain unchanged.

2. *Diffusion unit*

Dependent on the particular properties of different substances we have used diffusion tubes and vessels of different kind.

Diffusing the vapour of a volatile substance from a solution (*e.g.* hydrochloric acid in water) we made use of a large vessel (see Fig. 5a) containing much liquid, in order to keep the concentration nearly unchanged and the saturated vapour pressure nearly constant. Using simple liquids we prefer tubes of the kind as is shown in Fig. 5b.

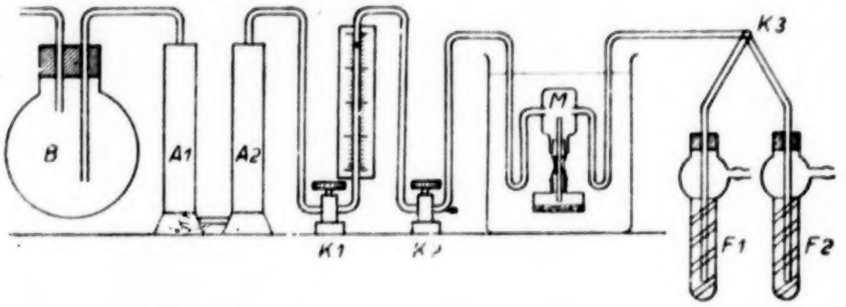


Fig. 4a. Flow diagram of the apparatus used.

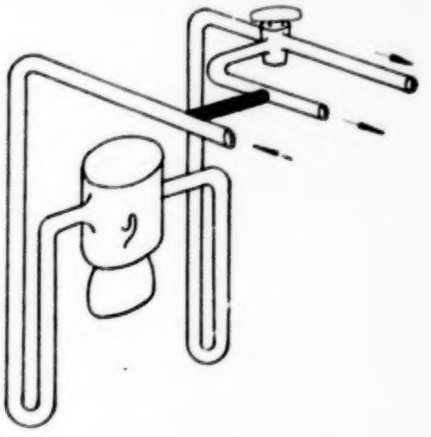


Fig. 4b. Vapour dosing apparatus.

The liquid phase of substances, possessing a great adhesion to glass, may sometimes creep along the inner wall of the tube. In this instance we used a combination as is shown in the Figs. 5c and 5d, consisting of desiccated glass. In Table III the dimensions of a number of tubes, used in our investigation, are shown. The geometrical factor $\frac{A}{l}$ varied roughly from 0.003 to 0.3.

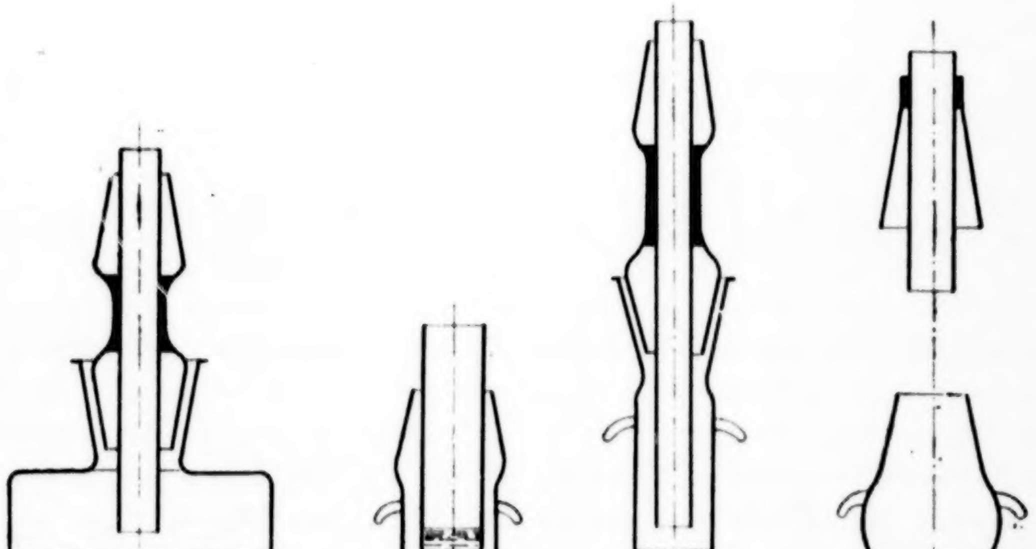


Fig. 5. Some diffusion tubes and liquid vessels of different kind.

SECONDARY FACTORS INFLUENCING THE QUANTITY OF THE VAPOUR DIFFUSED

The time required to establish conditions sufficiently close to the stationary state is approximately determined by Fick's second law:

$$\frac{\partial p}{\partial t} = \frac{\partial^2 p}{\partial x^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (24)$$

Assuming that the diffusion tube initially contains no vapour and that p_0 is the

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TABLE III

DIMENSIONS OF DIFFUSION TUBES USED

No.	*Length in cm* l	*Cross section in cm²* A	*open ends*	*Geometrical factor in cm* $\frac{A}{l}$
1	10.0	0.0315	2	0.00315
3	10.0	0.101	2	0.0101
4	10.0	0.211	2	0.0211
5	9.95	0.332	2	0.0333
8	5.0	1.69	1	—
9	15.1	0.332	2	0.0220
10	19.6	0.332	2	0.0170
11	30.1	0.332	2	0.0110
17	5.0	1.35	1	—

partial pressure of the saturated vapour, equation (24) must satisfy the boundary conditions:

$p = 0$ at $x = l$ for all values of t
$p = p_0$ at $x = 0$ when $t > 0$
$p = 0$ at $t = 0$ when $x > 0$

After integration of equation (24) and substitution of the boundary conditions mentioned, we obtain:

$$\frac{p}{p_0} = 1 - \frac{x}{l} - \frac{2}{\pi}\sum_{1}^{\infty}\frac{1}{n}\,e^{-n^2\mu t}\sin\frac{x}{l}n\pi \quad \ldots\ldots \quad (25)$$

$$\text{where: } \mu = \frac{\pi^2 D}{l^2} \quad \ldots\ldots\ldots\ldots \quad (25a)$$

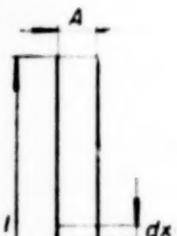

Fig. 6. A schematic reproduction of a diffusion tube.

The ratio ϑ of the quantities of vapour diffused respectively per unit of time after a time t and in the steady state may be written as:

$$\vartheta = \frac{\left(\frac{\partial p}{\partial x}\right)_{l,t}}{\left(\frac{\partial p}{\partial x}\right)_{l,\infty}} = 1 + 2\sum_{1}^{\infty}(-1)^n e^{-n^2\mu t} \quad \ldots\ldots \quad (26)$$

If a sufficient approach to the stationary state is reached, when $1 - \vartheta < 0.01$, then a calculation based on (26) shows that μt must be > 5. A stationary state will therefore be reached, when $t > \frac{l^2}{2D}$.

For average values taking $l = 10$ cm and $D = 0.1$ cm²/sec., we obtain $t > 500$ sec. In this case a stationary state may therefore be expected after about 10 minutes. It is obvious that a stationary state will be obtained more rapidly by using shorter tubes. In all cases where a low value of the maximum diffusion flow is needed, it is preferable to use narrow short tubes rather than wide long tubes.

Changes in pressure, temperature and rate of air flow in the diffusion unit, during an experiment, may alter the quantity of vapour, diffusing per unit of time.

The temperature should therefore be kept constant to within 0.1°C, the pressure to within 0.1%. Another source of errors may be the existance of a concentration gradient of the vapour in the liquid vessel. For this reason the distance between the surface of the liquid and the lower opening of the tube must be as small as possible (see Fig. 5a and 5c). Discrepancy may also occur as a result of turbulence in the diffusion tube. For this reason the rate of air flow should not be too much above 100 ml/min and the geometrical factor of the diffusion tube should not be much above 0.4 cm.

If the substance to be investigated shows the phenomenon of dissociation or association in the gaseous state this fact has to be taken into account.

For an accurate calculation of the diffusion flow the true values of the diffusion coefficient and the vapour pressure must be known.

EXPERIMENTAL RESULTS

In order to test the equations derived and to study the experimental difficulties, we have performed a number of experiments with hydrochloric acid (36% HCl) at 20°C and with propionic acid at different temperatures. The vapour containing air flow was passed into water (distilled and carbon dioxide-free) to absorb the vapour of the acid used. The hydrochloric acid was titrated with a $0.05N$ sodium hydroxide with methyl red as an indicator, the propionic acid with $0.01N$ sodium hydroxide and phenolphthalein as an indicator. The results of our experiments are shown in Figs. 7, 8 and 9.

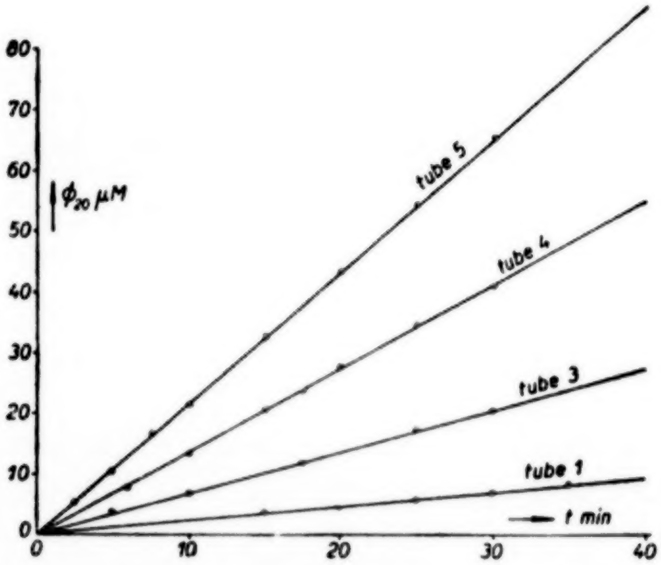

Fig. 7. The quantities of the HCl vapour transported by diffusion through tubes with different cross sectional areas and a length of 10 cm at 20°C, 1 atm and a rate of air flow of 100 ml/min. (Dimensions and numbers of tubes are given in Table III.)

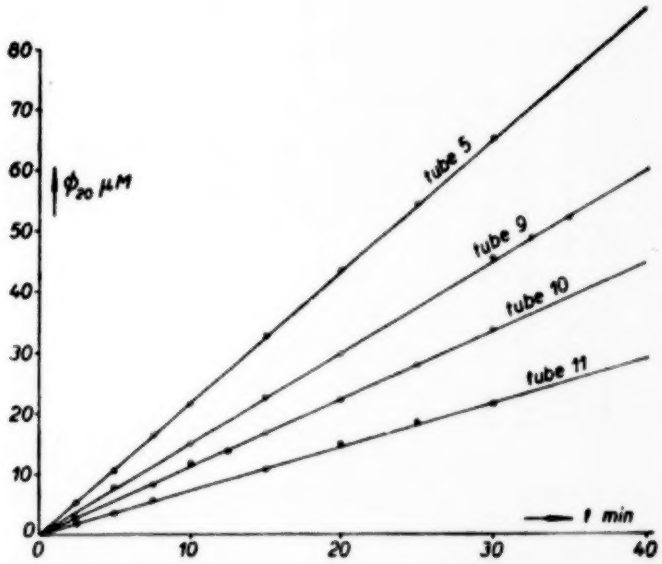

Fig. 8. The quantities of the HCl vapour transported by diffusion through tubes with different lengths and a cross sectional area of 0.332 cm² at 20°C, 1 atm and a rate of air flow of 100 ml/min. (Dimensions and numbers of tubes are given in Table III.)

The influences of the cross sectional areas and the length of the tubes are shown in the Figs. 7 and 8 respectively. The slopes of the lines in these figures correspond with the diffusion flows of hydrochloric acid (φ_{20}) per unit of time found experimentally.

In Fig. 9. the values (φ_{20}) of the slopes obtained in the Figs. 7 and 8 have been plotted against the geometrical factors $\left(\frac{A}{l}\right)$ of the tubes. Fig. 9. shows that there is a linear relationship between the diffusion flow and the geometrical factor for all 7 tubes under the conditions of the experiment.

Fig. 10 shows the results of our experiments at 20°C with tube 8 containing different volumes of propionic acid. The quantities of vapour diffused per unit of time (φ_{20}) have been plotted against the values of the geometrical factor $\left(\frac{A}{l}\right)$. Again a linear relationship is found between the diffusion flow and the geometrical factor whereas in this case a tube of the type given in Fig. 5b was used.

The influence of the temperature of the diffusion unit is shown in Fig. 11. We used tube 17 (type shown in Fig. 5b) containing about 1 ml of propionic acid; the geometrical factor was 1/3 cm. The quantities of propionic acid transported by diffusion through this tube are plotted against time at different temperatures of the diffusion unit. The slope of the line $\tau = 20°C$ (see Fig. 11) has however been calculated with data taken from Fig. 10.

In Table IV we have given the ratios $\varkappa_\tau$ of the unit flows at τ°C and 20°C. The experimental values given in Fig. 11 are used to calculate those of $\varkappa_\tau$. The values given in the third column are in good agreement with the calculated values given in the fourth column.

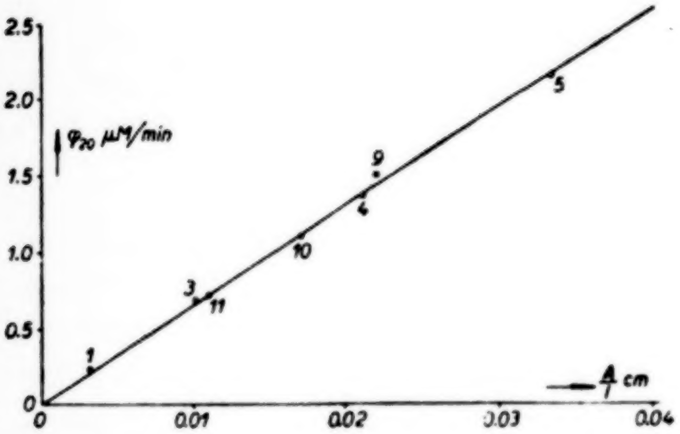

Fig. 9. The quantities of HCl vapour transported by diffusion per unit of time are plotted against the geometrical factors ($\frac{A}{l}$). The experiments were carried out at 20°C, 1 atm and a rate of air flow of 100 ml/min. (The dimensions of the corresponding tubes are given in Table III.)

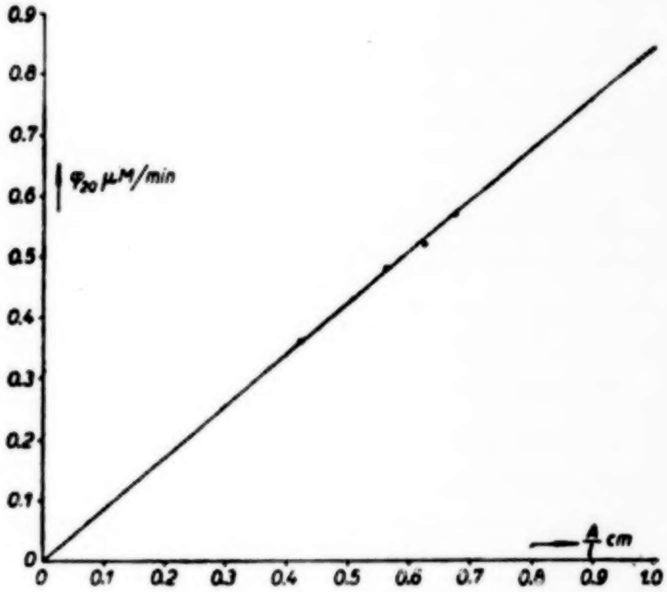

Fig. 10. The quantities of propionic acid vapour diffused per unit of time through tube 8 are plotted against the geometrical factor. The experiments were carried out at 20°C, 1 atm and a rate of air flow of 100 ml/min.

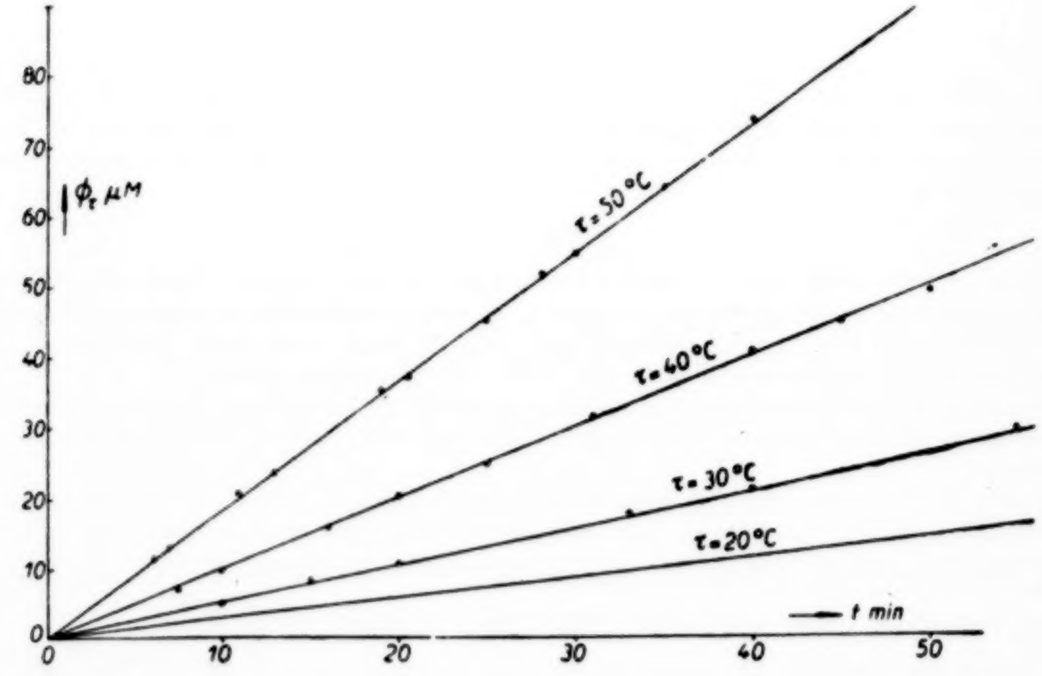

Fig. 11. The quantities of propionic acid, transported by diffusion at different temperatures through tube 17 with a geometrical factor $\frac{A}{l} = \frac{1}{3}$ cm. The total pressure was 1 atm and the rate of air flow 100 ml/min.

TABLE IV

RATIOS OF UNIT FLOWS AT τ°C AND 20°C

Temperature	$(\varphi_0)_\tau \frac{\mu mol}{cm\ min}$	$\varkappa_\tau = \frac{(\varphi_0)_\tau}{(\varphi_0)_{20}}$	
		exp. detmd. (Fig. 11)	*taken from lit. (Fig. 3)*
20°C	0.84	1.00	1.00
30°C	1.59	1.90	1.93
40°C	2.98	3.55	3.56
50°C	5.55	6.6	6.4

Experiments with mustard gas, trans-lewisite I and other organic substances show that the diffusion flows and concentrations experimentally found, agree with the values calculated in the way we have described.

OTHER APPLICATIONS OF THE DIFFUSION METHOD

Making use of equation (9) it is possible to calculate the vapour pressure p_0 for a substance from diffusion measurements which give the value for φ_0. It is obvious that the accuracy with which p_0 is obtained is dependent on the accuracy with which the diffusion coefficient D is known. In general the diffusion coefficient for a substance will not be known, but must be calculated using GILLIAND's formula. For this reason a high degree of accuracy is not to be expected but a sufficiently accurate value to allow at least a rough estimate of the vapour pressure may be obtained.

It is also possible to obtain values for both the diffusion coefficient D and the vapour pressure p_0 by carrying out diffusion measurements at several low rates of air flow and a high value of the geometrical factor. This method is only applicable in the case of substances with a low vapour pressure (*e.g.* $p_0 < 0.01\ p_t$). By carrying out diffusion experiments at different temperatures it is also possible to determine rough values for the heat of evaporation.

ACKNOWLEDGEMENT

I gratefully acknowledge the permission of the National Defence Research Council T.N.O. to publish the results of this investigation and also wish to express my thanks to the Director of the Laboratory of Chemical Research of this Council, Drs. J. VAN ORMONDT, for his constant interest in this study.

SUMMARY

To obtain air flows with low, constant and reproducible vapour concentrations, we have developed a dynamic method based on diffusion through a cylindrical tube at a fixed temperature. The quantities of the vapour diffused per unit of time have been calculated. In general these calculated values agree to within 10% with the observed values.

A very wide range of vapour concentrations is obtainable by taking tubes of different dimensions, by variation of the temperature of the diffusion unit and of the quantity of air mixed with the vapour.

The diffusion method requires a simple apparatus, has various advantages over other methods described in the literature and is especially suitable for the study of qualitative detection and quantitative determination of small amounts of vapour in atmospheric air.

RÉSUMÉ

Pour obtenir un courant d'air, avec une faible concentration de vapeur, constante et reproductible, l'auteur a établi une méthode dynamique, basée sur la diffusion à travers un tube cylindrique, à une température fixe. Les quantités de vapeur diffusées par unité de temps ont été calculées. En général, ces valeurs calculées correspondent à moins de 10% avec les valeurs observées.

On peut obtenir des concentrations de vapeur très diverses en utilisant des tubes de dimensions différentes et en faisant varier la température du diffuseur et la quantité d'air ajoutée à la vapeur.

Cette méthode de diffusion utilise un appareil simple; elle présente des avantages sur les autres méthodes décrites dans la littérature et convient spécialement pour l'étude de détections qualitatives et de déterminations quantitatives de faibles teneurs de vapeur dans l'air atmosphérique.

ZUSAMMENFASSUNG

Um einen Luftstrom mit einer kleinen, konstanten und reproduzierbaren Dampfkonzentration zu erhalten, wurde eine dynamische Methode entwickelt, welche auf Diffusion durch ein zylindrisches Rohr bei einer bestimmten Temperatur beruht. Die pro Zeiteinheit diffundierten Dampfmengen wurden berechnet. Diese berechneten Mengen sind im allgemeinen innerhalb 10% mit den experimentellen Werten im Einklang.

Die Dampfkonzentration kann innerhalb weiter Grenzen variiert werden durch Anwendung von Röhren verschiedener Dimensionen, durch Änderung der Temperatur des Dampfdosierapparates und indem man den Dampf mit verschiedenen Luftmengen mischt.

Die Diffusionsmethode erfordert einen einfachen Apparat, hat verschiedene Vorteile gegenüber anderen in der Literatur beschriebenen Verfahren und ist sehr geeignet für das Studium des qualitativen Nachweises und der quantitativen Bestimmung kleiner Dampfkonzentrationen in atmosphärischer Luft.

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THE THERMAL DECOMPOSITION OF SOME METAL CHELATES OF 5.7-DIIODO-8-QUINOLINOL (IODOXINE)

by

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INTRODUCTION

Although a great deal of work has been done on the use of 8-quinolinol (oxine) as a precipitant for metal ions in solution, very little interest has been shown concerning the analytical applications of the 5.7-dihalogenated derivatives. The introduction of chlorine, bromine or iodine in the 8-quinolinol molecule does not alter the functional group so it might be expected that they would precipitate the same metal ions. This has indeed been found to be the case[1].

5.7-Dichloro-8-quinolinol (chloroxine) and 5.7-dibromo-8-quinolinol (bromoxine) were introduced as organic analytical reagents by BERG[2,3]. It was found that the chelates formed with the halogenated derivatives possessed greater stability in acid solutions than with 8-quinolinol. Besides this, much better gravimetric factors were found because of the increased molecular weight of the chelates. Recently, a preliminary study was reported on the use of 5.7-diiodo-8-quinolinol (iodoxine) as a precipitant for various metal ions[4]. A method was proposed for the gravimetric determination of copper(II) and it was also suggested that this reagent might also be used for the colorimetric determination of several metal ions.

The precipitates of a number of metals with 5.7-dichloro-8-quinolinol and 5.7-dibromo-8-quinolinol have been studied on the thermobalance by DUVAL[5] and by the author[6]. No general statement can be made concerning the thermal stability of the halogenated derivatives as compared to the unsubstituted chelates. In some cases the thermal stability was greater, while in others it was considerably lower.

The chelates of 5.7-diiodo-8-quinolinol have not previously been studied on the thermobalance. Thus, it was of interest to subject the chelates of scandium, thorium, uranium(VI), copper(II), nickel, lanthanum, and iron(III) to thermogravimetric pyrolysis.

EXPERIMENTAL

Chemicals

5.7-Diiodo-8-quinolinol was obtained from the Aldrich Chemical Co., Inc., Milwaukee 12, Wisc. It was used without further purification.

The sources of the uranium, scandium and thorium salts has previously been described[7]. All other chemicals used were of C.p. reagent grade quality.

Thermobalance

The construction and operation of the thermobalance has previously been described[8]. The sample sizes ranged from 100 to 150 mg. The heating rate for all samples was constant at 4.5°/min.

Preparation and thermolysis of the chelates

The metal ions were precipitated from aqueous solution at a pH of 5-7. The procedure consisted of adding a slight excess of the reagent (1.5 g of 5.7-diiodo-8-quinolinol in 100 ml of dioxane) to 100 ml of solution containing about 0.1-0.2 g of the metal salt and 10 ml of a 2*N* ammonium acetate solution. The metal ions precipitated immediately on introduction of the reagent. The precipitated chelates were collected on sintered porcelain crucibles, using suction, washed several times with water and then with dioxane to remove any excess of reagent. The chelates were air dried for 24 h before pyrolysis on the thermobalance.

DISCUSSION

5.7-Diiodo-8-quinolinol

Compared to the 5.7-dichloro and the 5.7-dibromo derivatives, 5.7-diiodo-8-quinolinol is the least stable thermally. As can be seen in Fig. 1, the compound began to sublime slightly at 135°. On further heating, the substance decomposed rapidly. At 310° a black charred mass remained in the thermobalance pan and this oxidized gradually until at 700° the pan was empty. In many respects, the behavior was identical to the 5.7-dibromo derivative[6]. However, the 5.7-diiodo derivative showed even less tendency to sublime but decomposed instead. This inability to sublime at elevated temperatures makes it necessary to remove any coprecipitated reagent by washing with dioxane before drying. This, of course, may be an obvious disadvantage to the use of this reagent.

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Copper 5.7-diiodo-8-quinolinol

The copper chelate possessed the greatest thermal stability of all of the chelates studied. As shown in Fig. 1, the first slight loss in weight occurred at 165°. On further heating, the chelate decomposed quite rapidly until at 455° the oxide level, CuO, appeared. The drying temperature suggested by MUKHERJEE AND BANERJEE[4] of 110-120° is correct but too restricted. The gravimetric factor is 9.30% CuO for the chelate, $Cu(C_9H_4I_2NO)_2$.

Nickel 5.7-diiodo-8-quinolinol

The nickel chelate was much less stable than the corresponding copper chelate. Fig. 1 shows that the first weight loss occurred at 80°. A horizontal appeared at 155-210° but the composition did not correspond to any known stoichiometry. At 390° the chelate began to decompose rapidly, giving the oxide level, NiO, beginning at 505°.

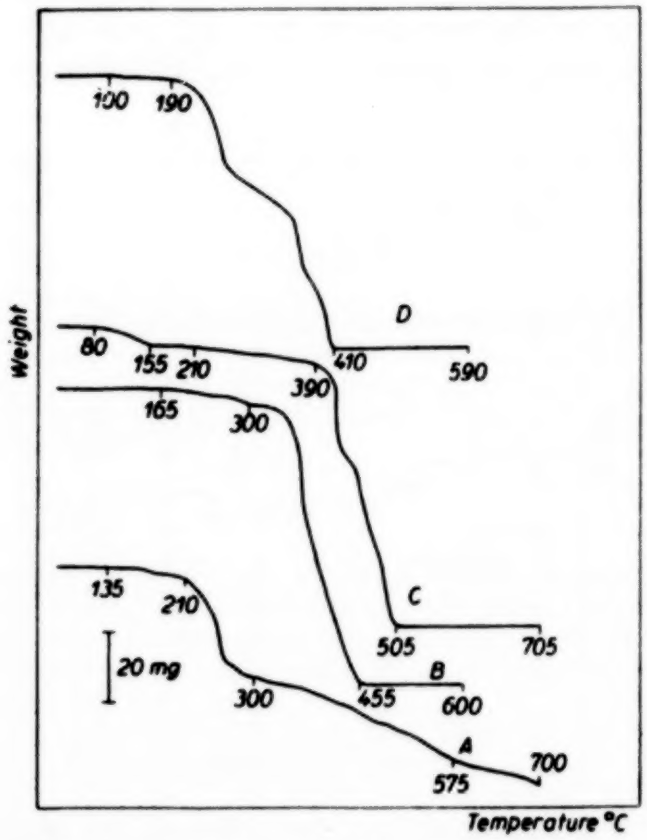

Fig. 1. The thermal decomposition of the 5.7-diiodo-8-quinolinol chelates.
A. 5.7-Diiodo-8-quinolinol.
B. Copper(II) 5.7-diiodo-8-quinolinol chelate.
C. Nickel 5.7-diiodo-8-quinolinol chelate.
D. Iron(III) 5.7-diiodo-8-quinolinol chelate.

Iron (III) 5.7-diiodo-8-quinolinol

The thermal decomposition curve is shown in Fig. 1. The chelate was stable up to 100°. Beyond 190° the chelate decomposed rapidly to give the oxide level, Fe_2O_3, beginning at 410°.

Lanthanum 5.7-diiodo-8-quinolinol

Although the precipitation of lanthanum was not previously suggested[4], it was found that an insoluble chelate was formed with the reagent. The other rare earth metal ions would probably also form the same type of chelates. The lanthanum chelate was the least stable of all the chelates studied. The chelate began to decompose at 65°

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with the rate of decomposition increasing to a rapid rate beginning at 145°. The oxide level, La_2O_3, appeared at 585°. The use of this chelating agent might compare quite favorably with that of 8-quinolinol as previously studied[7].

Scandium 5.7-diiodo-8-quinolinol

One of the most interesting types of chelates formed between 8-quinolinol and certain metal ions are those with scandium, thorium, and uranium(VI). These chelates can be represented by the general formula $M(Ox)_n \cdot HOx$; where M is the metal ion of oxidation state *n* and HOx the 8-quinolinol molecule. From the formula it can be seen that the chelate contains an extra molecule of chelating agent which is thought to be held by weak lattice forces. The 5.7-dichloro and 5.7-dibromo derivatives also form the same type of chelates.

The 5.7-diiodo derivative, however, under the conditions of precipitation used in this study, gave only the normal chelate, $Sc(C_9H_4I_2NO)_3$. From Fig. 2 it can be seen that this chelate began to decompose at 75°. At 250° the rate of decomposition increased quite rapidly until the oxide level, Sc_2O_3, appeared at 525°.

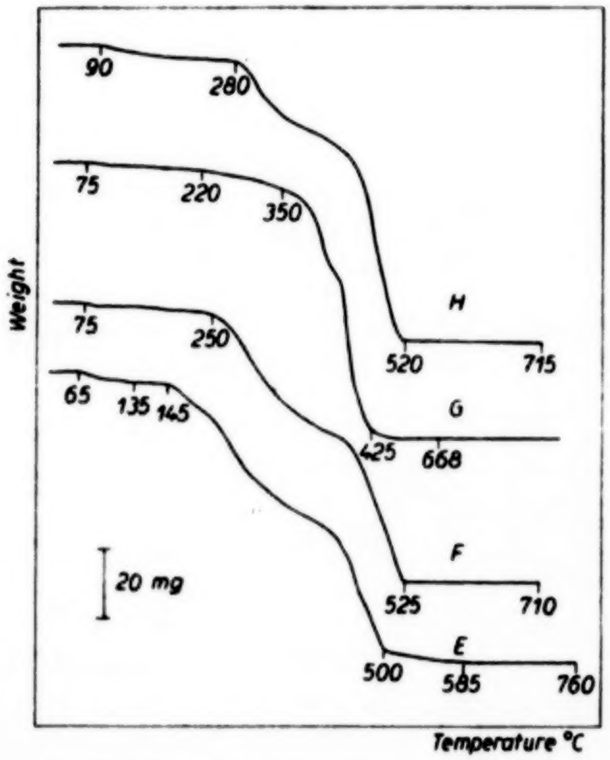

Fig. 2. The thermal decomposition of the 5.7-diiodo-8-quinolinol chelates.
E. Lanthanum 5.7-diiodo-8-quinolinol chelate. G. Uranium(VI) 5.7-diiodo-8-quinolinol chelate.
F. Scandium 5.7-diiodo-8-quinolinol chelate. H. Thorium 5.7-diiodo-8-quinolinol chelate.

Uranium(VI) 5.7-diiodo-8-quinolinol

The uranium chelate, in contrast with scandium, did contain an extra molecule of the reagent, $UO_2(C_9H_4I_2NO)_2 \cdot C_9H_4I_2NOH$. However, like the uranium chelates with the 5.7-dichloro and the 5.7-dibromo derivatives[6], the extra molecule cannot be removed by heating. The chelate, as shown in Fig. 2, began to decompose at 75°. The decomposition increased rapidly above 350° until the oxide level, U_3O_8, appeared at 668°.

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Thorium 5.7-diiodo-8-quinolinol

Thorium, like scandium, precipitated as the normal chelate, $Th(C_9H_4I_2NO)_4$, under the conditions of this study. Fig. 2 shows that the chelate was stable up to 90° where it began to decompose slowly. At 280° the decomposition increased rapidly until the oxide level, ThO_2, appeared at 520°.

To summarize, the temperature limits for all of the chelates are given in Table I.

TABLE I

TEMPERATURE LIMITS FOR THE 5.7-DIIODO-8-QUINOLINOL CHELATES*

Metal	*Chelate formula*	*Chelate temperature limit °C*	*Oxide temperature limit °C*
HIOx**	HIOx	135	—
Copper(II)	$Cu(IOx)_2$	< 165	> 455
Nickel	$Ni(IOx)_2$	< 80	> 505
Iron(III)	$Fe(IOx)_3$	< 100	> 410
Lanthanum	$La(IOx)_3$	< 65	> 585
Scandium	$Sc(IOx)_3$	< 75	> 525
Uranium(VI)	$UO_2(IOx)_2 \cdot HIOx$	< 75	> 668
Thorium	$Th(IOx)_4$	< 90	> 520

* Heating rate of 4.5°/min.

** 5.7-Diiodo-8-quinolinol.

SUMMARY

The thermal decomposition of the chelates of 5.7-diiodo-8-quinolinol (iodoxine) with copper(II), nickel, iron(III), lanthanum, scandium, uranium(VI) and thorium was studied on the thermobalance. It was found that the chelates varied greatly in stability. The least stable began to decompose at 65° while the most stable began at 165°. The oxide levels were obtained in the temperature range of 410 to 668°.

RÉSUMÉ

La décomposition thermique des chélates de la 5.7-diiodo-8-hydroxyquinoléine (iodoxine) avec le cuivre(II), le nickel, le fer(III), le lanthane, le scandium, l'uranium(VI) et le thorium a été étudiée sur la thermobalance. La stabilité varie beaucoup d'un chélate à l'autre. Le moins stable commence à se décomposer à 65°, tandis que le plus stable à 165°. Les paliers des oxydes ont été obtenus entre 410 et 668°.

ZUSAMMENFASSUNG

Die thermische Zersetzung der Chelate von 5.7-Dijodo-8-hydroxychinolin (Jodoxin) mit Kupfer(II), Nickel, Eisen(III), Lanthan, Scandium, Uran(VI) und Thorium wurde auf der Thermowaage untersucht. Die Stabilität dieser Chelate ist sehr verschieden; die Zersetzung des Labilsten beginnt bereits bei 65°, während diejenige des Stabilsten erst bei 165° einsetzt. Die Oxydstufen wurden bei 410 bis 668° gefunden.

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THE SEPARATION OF IRON VALENCIES BY PAPER CHROMATOGRAPHY

by

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INTRODUCTION

It is well known that Fe is an essential element for plant and animal growth; one of its roles in metabolism is associated with the cytochromes which contain the metal in both ferrous and ferric states.

The separation of the valency states of Fe by paper chromatography was undertaken as a preliminary to the investigation of the role of these valency changes in biological systems.

POLLARD[1] first reported a separation of Fe^{+2} and Fe^{+3} as chlorides by upward chromatography on paper strips using an ether-methanol-hydrochloric acid-water eluant in which the R_F values differed by 0.35.

In this paper the separation of Fe^{+2} and Fe^{+3} in acetate-buffered solution is described. Downward chromatography in an *n*-butanol-ethanol-acetic acid-water system was employed, and differences in R_F value of up to 0.67 were observed. The separation also appeared to be quantitative for the amounts employed.

EXPERIMENTAL

Construction of Fe calibration graph

Standard Fe^{+3} solution was prepared by dissolving 0.864 g of AnalaR ferric ammonium sulphate in water, adding 10 ml of 10*N* hydrochloric acid, and diluting the solution to 1000 ml with distilled water. 1 ml of this solution contained 100 μg of Fe. To different volumes of this ferric standard ranging from 0.5 ml to 4 ml, 10 ml of a 20% w/v solution of KCNS in 2*N* HCl was added, and the mixture extracted by shaking with 50 ml of a mixture of amyl alcohol and ether (100:40)[2]. The extracts were filtered (Whatman No. 41 paper) and readings obtained on a Hilger "Spekker' with a drum-setting of 1.30, using 0.5 cm cells and Ilford No. 604 green filters.

Preparation of Fe solutions for chromatography

The Fe^{+2} solution was prepared by dissolving about 1.25 g of $FeSO_4 \cdot 7H_2O$ (AnalaR) with 2-3 drops of sulphuric acid in 80-90 ml of water, buffering the solution to pH 4 with a saturated solution of sodium acetate trihydrate using B.D.H. Universal Indicator Paper, and diluting to 100 ml. 1.241 g of $FeSO_4 \cdot 7H_2O$ gave a final concentration of 2500 μg Fe per ml.

The Fe^{+3} solution was prepared in an exactly parallel manner using 2.1525 g of $FeNH_4 \cdot (SO_4)_2 \cdot 12H_2O$ (mol. wt. = 482) to give a final concentration of 2500 μg Fe per ml. Both valency solutions were buffered and diluted to 100 ml immediately before use as, on standing, basic acetates tended to separate especially with Fe^{+3}.

The strengths of the Fe solutions were checked by digesting 0.1 ml aliquots with HNO_3 (AnalaR 25 ml) and $HClO_4$ (AnalaR 60%, 2 ml) until the latter began to fume off. The mixture was cooled, 5 ml of water added, followed by 50 ml of 20% w/v KCNS in 2*N* HCl and the red colour of the ferric thiocyanate extracted into 50 ml of amyl alcohol-ether as before. The lower aqueous layer containing precipitated $KClO_4$ was run off, and the extract filtered and "Spekkered" as previously described.

The HNO_3-$HClO_4$ digestion could be avoided by evaporating the aliquots with 10*N* HCl (4 ml) and 10 volume H_2O_2 (16 ml) until the volume of the solution was about 5 ml and all H_2O_2 had been expelled; after the addition of the 50 ml of KCNS reagent the colorimetric determination was carried out as described above.

Separation of the valencies by paper chromatography

Downward chromatography was employed with sheets of Whatman No. 1 filter paper which had previously been washed with 2*N* HCl (30 minutes soak) and distilled water. The eluant consisted of 40 ml *n*-butanol, 25 ml ethanol, 25 ml glacial acetic acid and 35 ml water, and it was necessary to allow the eluant to stand in the chromatography tank (40 × 22 × 51 cm) during the night preceeding a run to obtain equilibration of the atmosphere inside the vessel.

0.1 ml of each valency solution, buffered to pH 4, were superimposed along the "starting line" on a chromatogram and allowed to dry*. The chromatogram was allowed to remain in the tank for about 2½-3 hours until the eluant had travelled 16-17 cm. After drying at room temperature the paper was exposed to steam from a flask of boiling water containing a small quantity of oxine. The latter was vaporized, and detected the valencies as greenish-black bands. This modified procedure was adopted because a pilot-spot was not always an accurate guide to the depth of the band on the main chromatogram. If the latter was dipped in, or sprayed with reagent solutions, there was always the risk of contamination, or loss of material from the paper.

R_F values were approximately 0.2-0.3 for Fe^{+2} and 0.8-0.9 for Fe^{+3}. In mixtures where the concentration of $Fe^{+2} \gg Fe^{+3}$, the difference in *R_F* value was not as great (0.2 for Fe^{+2}, and 0.6 for Fe^{+3}).

The concentration of Fe in the valency bands was determined by ashing the excised portions of the paper with HNO_3 (25 ml) and $HClO_4$ (2 ml), and determining the Fe colorimetrically in the manner already described. A "blank" estimation on the acid gave a value of 7 µg Fe. The same value was also obtained when a "blank" chromatogram was treated as one bearing Fe valencies. In this case a "pilot" strip was run and the corresponding area of paper excised from the main chromatogram and wet-ashed. This showed that acid-washing had rendered the sheets remarkably low in Fe.

Some results are given in Table I.

TABLE I

	µg Fe^{+2} run	*µg Fe recovered*	*µg Fe^{+3} run*	*µg Fe recovered*
Expt. 1	249	255	263	262
,, 2	249	257	263	263
,, 3	243	249	250	251
,, 4	243	250	250	252

Thus for the quantities employed, and in view of potential sources of error attending an Fe estimation by chromatography (*e.g.* specks of rust on benches, and occasionally embedded in filter papers *etc.*), the separation appears to be quantitative. The "blank" determination on the paper is not truly representative because a different sheet of paper has to be used.

When the valency bands were heated with HCl and H_2O_2 as described above, the paper was broken down into a suspension, but not completely destroyed. The subsequent determination of Fe by the addition of the KCNS reagent and extraction into alcohol-ether yielded very low values for both valencies. If H_2O_2 was added to the lower aqueous layer, and the latter extracted with a fresh portion of amyl alcohol-ether, a further quantity of ferric thiocyanate could be obtained. It appeared that a considerable amount of Fe was reduced of the ferrous state by this method of digestion, and a brief investigation was carried out to obtain a possible explanation of this phenomenon.

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* This was essential for a good separation.

A portion of acid-washed Whatman No. 1 paper 100-110 cm^2 in area (about the same area as an Fe-bearing strip) was digested with 10*N* HCl (4 ml) and 10 volume H_2O_2 (16 ml) until the volume of the mixture was about 10 ml. An equal volume of water was added, and the solution filtered free of cellulose. The residue was washed with 5 ml of water. The combined filtrates were evaporated to dryness in a vacuum desiccator over NaOH, and the residue taken up in 2 ml of water. This solution was spotted onto strips of No. 54 filter paper and run at 50° overnight in an eluant of *n*-butanol saturated with water at room temperature. When the dried chromatogram was developed with *p*-anisidine hydrochloride, a strong glucose spot (confirmed by running spots of glucose, and also fructose and sucrose alongside) appeared on the paper. The cellulose hydrolysate also gave a weak spot, which may be a pentose, at an R_F value $>$ R_F value of glucose, and several weak spots of low R_F value, which were possibly di- and trisaccharides.

A fresh cellulose hydrolysate was prepared as above, and the combined filtrates neutralized with a strong solution of NaOH, and made slightly acid with 2*N* HCl. The solution was diluted to 40 ml and 2 ml aliquots taken for sugar analysis by the Somogyi-Nelson arseno-molybdate method. It was estimated that 30-50 mg of glucose was released from this area of paper when subjected to the above treatment. If the digestion was done without H_2O_2 only a trace of reducing substance was found.

The reducing action of glucose upon Fe^{+3} was studied by boiling a solution of 2000 μg of Fe^{+3} in 2*N* HCl with 0.4 g of glucose for 5-10 min. The solution was buffered with sodium acetate to pH 4 and 0.2 ml of the mixture spotted onto a chromatogram, dried, and run in the *n*-butanol-ethanol-acetic acid-water eluant used for the valency separations. When the dried chromatogram was developed with 8-hydroxyquinoline (carried in steam) a considerable Fe^{+2} zone appeared above the Fe^{+3} band. No Fe^{+2} band appeared when control solutions containing (1) Fe^{+3} and glucose, but not heated, or (2) Fe^{+3} boiled without glucose, were subjected to the same analysis. From these results it was thought probable that the low Fe recovery from a cellulose hydrolysate was due to the reduction of some of the metal to Fe^{+2} by the glucose released from the paper under treatment.

Ferrous oxinate

To the author's knowledge, a preparation and study of this compound has not yet been carried out, although its existence has been suggested by the work of JOHNSTON AND FREISER[3], and of MALEY AND MELLOR[4].

When a paper strip upon which Fe valencies have been separated was developed by dipping it into a solution of 8-hydroxyquinoline in ether and allowing it to dry in the air, a black stain appeared with Fe^{+3}, but a transient red colour, soon darkening and becoming black, was obtained with Fe^{+2}. A brick-red powder, purporting to be ferrous oxinate dihydrate was obtained by treating ferrous sulphate solution with ethanolic oxine in the absence of air according to the following method.

250 ml of water was placed in a 500 ml conical flask, and all air expelled by a rapid stream of CO_2. The stream of gas was maintained while sodium dithionite (1 g) was added; when this had dissolved, a solution of 0.5 g of $FeSO_4 \cdot 7H_2O$ (with 2 drops of H_2SO_4) in 5 ml of distilled water was run into the flask followed by 12 ml of a cold saturated solution of 8-hydroxyquinoline in ethanol. The temperature of the mixture was then raised to 95-100° until no more sulphurous vapours could be detected in the CO_2 issuing from the vessel (15-20 minutes). The flask was cooled in the gas stream, and the brick-coloured precipitate filtered off through a Büchner funnel using a Whatman 41 filter paper. The solid was washed quickly with distilled water, then ether, and dried in a stream of CO_2 at room temperature for an hour or so, finishing off in a vacuum desiccator over P_2O_5 for 1 day.

The product was a brick-red powder stable in air when dry. It dissolved readily in warm 5*N* HCl, and HNO_3 giving clear solutions which yielded no precipitate with a solution of $BaCl_2$, showing that SO_4^{-2} ions were not present in the complex.

When the compound was decomposed by KCNS and $2N$ HCl at room temperature in the absence of air (displaced by CO_2) a pink solution was obtained. On adding a few drops of H_2O_2, the solution became blood-red, suggesting that Fe^{+2} ions were the predominant cations liberated initially from the complex.

When heated in a stream of CO_2 in a glycerol bath, the solid darkened in colour at 80°, but decomposition appeared to begin at 110° yielding ferric oxinate.

The complex was insoluble in water, ether, chloroform, carbon tetrachloride, ethanol, acetone, benzyl alcohol, petrol ether and nitrobenzene (cold), but dissolved in dioxan, piperidine, and to a lesser extent in quinoline. It was however readily dissolved by pyridine (in which the Fe^{+3} compound is only slightly soluble), and the absorption spectrum from 300-600 mμ was plotted using pyridine as solvent. A maximum was found at 400 mμ and a minimum at 350 mμ. This is in contrast to the Fe^{+3} compound which gave maxima at 575 mμ and 470 mμ and a minimum at 415 mμ. The spectrum could not be plotted below 300 mμ owing to the behaviour of the pyridine in this wavelength range. The absorption spectra of the Fe^{+2} and Fe^{+3} oxinates are shown graphically in Fig. 1.

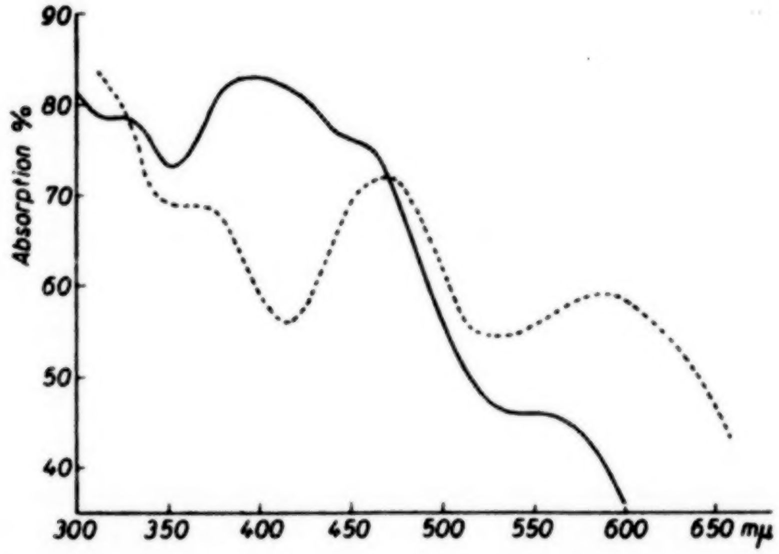

Fig. 1. Absorption Spectra of Fe oxinates in pyridine.
———— Fe^{+2} oxinate
– – – – Fe^{+3} oxinate

Analysis of Fe^{+2} oxinate

The percentage of Fe in the compound was estimated by wet-ashing 120-125 mg of the oxinate with HNO_3 (10 ml) and $HClO_4$ (2 ml) until the latter started to fume off. The digest was then cooled and diluted to 100 ml with water.

Aliquots of 1 ml were then mixed with 10 ml of a 20% w/v solution of KCNS in $2N$ HCl and extracted by shaking with 50 ml of redistilled ethyl acetate. The colours of the filtered extracts were then measured on a Hilger "Spekker" using 0.5 cm cells and Ilford No. 604 green filters after the calibration of the instrument with a series of standards ranging from 1-8 μg Fe per ml ethyl acetate. A mean value of 14.5% Fe was found.

The method was checked by wet-ashing 170-175 mg of Fe^{+3} oxinate, and proceeding as described. In duplicate experiments, values of 11.53% and 11.53% Fe were obtained; the theoretical value is 11.47%.

Complete analysis for the Fe^{+2} compound gave the percentage composition: Fe 14.5, C 57.3, H 4.4, N 7.6.

Bocquet and Paris[5] state that the oxinates of the bivalent ions of Mn, Co and Ni contain 2 molecules of water per molecule of oxinate. Calculated for $Fe(C_9H_6ON)_2 \cdot 2H_2O$ the percentages are: Fe 14.7, C 57.0, H 4.2 and N 7.4. This formula is therefore suggested by the author to be a probable one.

Water appears to be readily lost from the oxinate dihydrates of Mn, Co and Ni upon heating the complexes[5,6]. This seems to occur also with the ferrous complex (at 110°), which then passes into the ferric, as this valence state is the more stable when bound co-valently.

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SUMMARY

The quantitative separation of a mixture of Fe valency-states, in acetate-buffered solution, by paper chromatography in a *n*-butanol-ethanol-acetic acid-water eluant is described. Fe fractions were estimated as ferric thiocyanate which was extracted into amyl alcohol-ether. Complete ashing of the paper by HNO_3 and $HClO_4$ was necessary, as partial destruction with H_2O_2 and HCl reduced some iron to the Fe^{+2} state (probably by glucose released from the cellulose during digestion) and caused low results. The preparation and some properties of a ferrous-8-hydroxyquinoline complex are also described. Analysis of the complex suggested the formula $Fe(C_9H_6ON)_2 \cdot 2H_2O$.

RÉSUMÉ

La séparation quantitative du fer(II) et du fer(III) est décrite; elle s'effectue en solution tampon à l'acétate, par chromatographie sur papier en utilisant comme éluant le mélange *n*-butanol-éthanol-acide acétique-eau. Les fractions de fer sont déterminées comme thiocyanate ferrique, qui est extrait dans le mélange alcool amylique-éther. Une complète minéralisation du papier au moyen de HNO_3 et $HClO_4$ est nécessaire, une destruction partielle par H_2O_2 et HCl réduisant une partie du fer à l'état bivalent (probablement à cause du glucose provenant de la cellulose, lors de la digestion) et donnant des résultats faibles. La préparation et quelques propriétés d'un complexe fer(II)-hydroxy-8-quinoléine sont également décrites. L'analyse du complexe permet d'arriver à la formule $Fe(C_9H_6ON)_2 \cdot 2H_2O$.

ZUSAMMENFASSUNG

Die quantitative Trennung von zwei- und dreiwertigem Eisen in Acetatpufferlösung durch Papierchromatographie und mit einer Mischung von *n*-Butanol-Äthanol-Essigsäure-Wasser als Elutionsmittel wird beschrieben. Die Eisenfraktionen werden als Ferrithiocyanat bestimmt, welches mit Amylalkohol-Äther extrahiert wird. Eine vollständige Veraschung des Papiers mit HNO_3 und $HClO_4$ ist notwendig, da eine teilweise Zerstörung mit H_2O_2 und HCl einen Teil des Eisens zum zweiwertigen Zustand reduziert (wahrscheinlich durch aus der Zellulose entstandene Glukose) was niedrige Ergebnisse zur Folge hat. Die Herstellung und einige Eigenschaften eines Ferro-8-Hydroxychinolin-Komplexes werden beschrieben. Die Analyse dieses Komplexes führt zur Formel $Fe(C_9H_6ON)_2 \cdot 2H_2O$.

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PAPER CHROMATOGRAPHY OF INORGANIC IONS
XV. R_F VALUES IN MIXTURES OF BUTANOL AND HBr *

by

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For a number of years work has been proceeding in this laboratory to study systematically the behaviour of inorganic ions by paper chromatography. For many purposes such as radiochemical investigations it is important to know the R_F values of as many ions as possible in one given solvent.

Butanol saturated with hydrochloric acid was the first solvent completely investigated[1]. CARVALHO[2] extended this study to several butanol-hydrochloric acid mixtures. The results of this study showed so many applications that further investigations seemed justified.

While the complex chemistry of hydrochloric acid solutions had been studied by ion exchange[4] and solvent extraction[5], less work has been carried out with hydrobromic acid in spite of the very promising results of IRVING AND ROSOTTI[6] with ether extractions from aqueous hydrobromic acid. HERBER AND IRVINE[7] carried out anion exchange separations in hydrobromic acid solutions but had to limit the concentration of hydrobromic acid to less than $7M$ to avoid attack of the resin (Dowex-1).

The system butanol saturated with hydrobromic acid (10% aqueous solution) was examined some time ago[3]. In this paper we shall describe a more extensive work with mixtures of butanol and hydrobromic acid involving many ions.

Essentially the same information may be obtained from either ion exchange equilibria, partition coefficients and R_F values as we shall illustrate for the elements Ga(III), Tl(III) and In(III) in Fig. 1. In this work interesting data on the complex formation of the following elements were obtained: Cu(II), Te(IV), Pb(II), Ga(III), In(III) and Rh(III), also U(IV) and ReO_4^- whose behaviour in hydrobromic acid have presumably not been examined previously.

Most other elements differ little in chromatographic behaviour from hydrochloric to hydrobromic acid and satisfactory separations may be obtained in either butanol-hydrochloric or butanol-hydrobromic acid mixtures.

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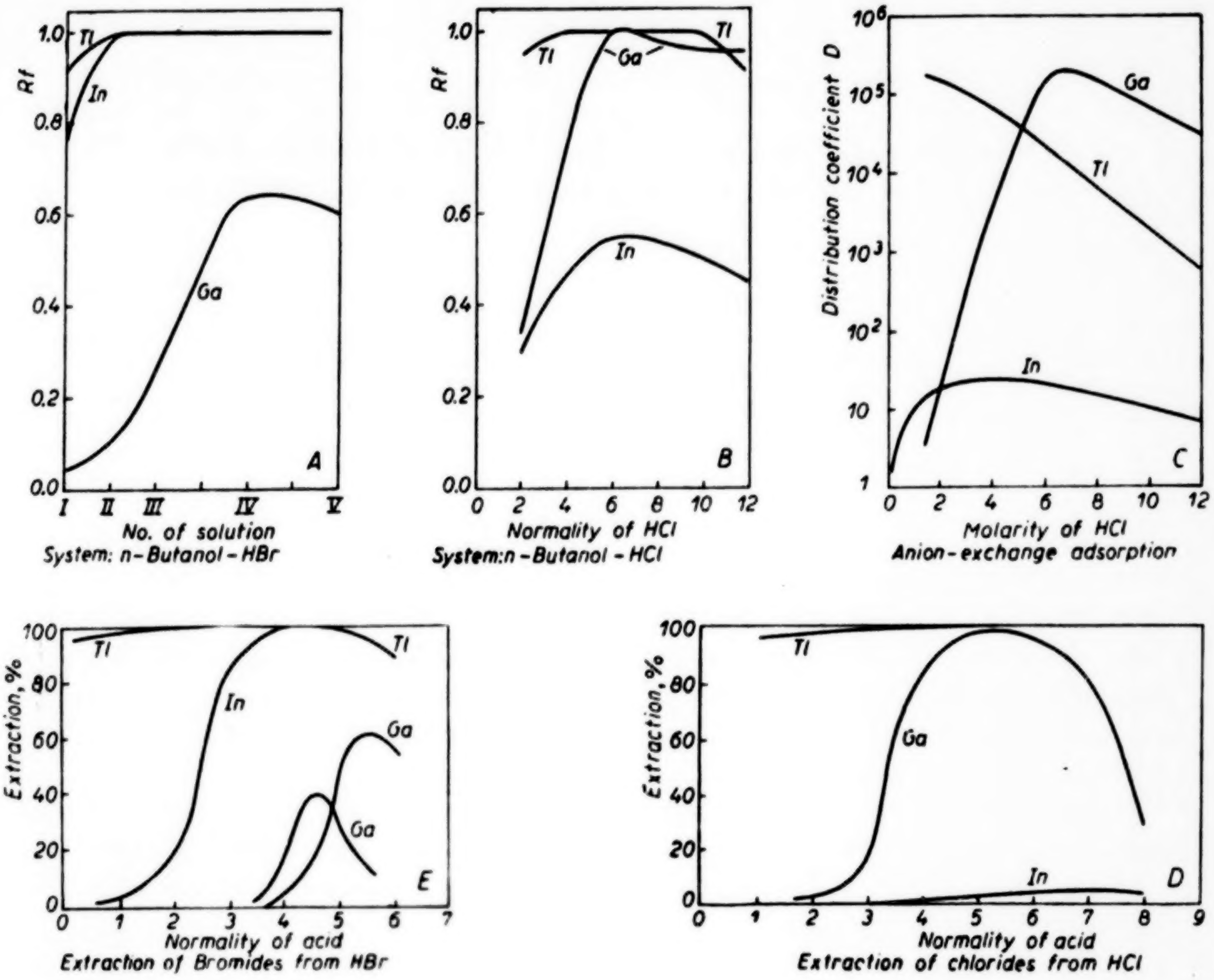

Fig. 1.

The R_F values, ion-exchange equilibria and partition coefficients for Ga(III), Tl(III) and In(III).

A. results of this study (paper chromatography)
B. results from Carvalho[2] (paper chromatography)
C. results from Kraus *et al.*[4] (adsorption on Dowex-1)
D. and E. results from Irving and Rosotti[6] (extraction with ethyl ether)

EXPERIMENTAL

Apparatus and procedure. The development was carried out by the ascending technique. Glass chromatography jars 36 cm high and 15 cm in diameter were used with glass covers. In two phase solvents the atmosphere was saturated with all constituents by placing a beaker containing the aqueous phase at the bottom of the jar.

The paper used was Whatman No. 1 in sheets 30 cm long and 30 wide. These were developed overnight for 16 (± 1) h at a room temperature of 22°C (± 2°).

Solvents. The hydrobromic acid (∼ 40%) and the normal butanol were Prolabo — Rhone Poulenc products of "pour analyses" purity and were employed without further purification. (Some of the experiments were carried out using a commercial quality hydrobromic acid.)

The following five solvents were prepared:

I. Butanol 100 ml + hydrobromic acid 10 ml + water 90 ml (two phases)
II. Butanol fraction of solvent I + hydrobromic acid 10 ml (one phase)
III. ,, ,, ,, ,, I + ,, ,, 20 ml ,, ,,
IV. ,, ,, ,, ,, I + ,, ,, 40 ml ,, ,,
V. ,, ,, ,, ,, I + ,, ,, 60 ml ,, ,,

The solvents were used after 24 h standing in the chromatography jars.

Solutions of the ions examined. In order to avoid interferences caused by the presence of other anions than bromides, the salts used were converted to bromides in each case. 10 ml of a 1% solution of the ion was prepared.

TABLE I

THE *R_F* VALUES

No.	*Ion*	*Solvent mixtures*					*Method of detection*
		I	*II*	*III*	*IV*	*V*	
1	K	0.04	0.11				2
2	Rb	0.04	0.11				2
3	Cs	0.04	0.11				2
4	Be	0.33	0.46	0.52	0.61	0.66	1
5	Mg	0.08	0.16	0.24	0.37	0.45	1
6	Ca	0.04	0.08	0.12	0.19	0.25	1
7	Sr	0.01	0.04	0.07	0.13	0.15	3
8	Ba	0.01	0.02	0.04	0.06	0.08	3
9	Zn	0.74	1.00	1.00	1.00	1.00	1
10	Cd	0.80	1.00	1.00	1.00	1.00	4,5
11	Hg(II)	1.00	1.00	1.00	1.00	1.00	4
12	Cu(II)	0.10	1.00	1.00	1.00	1.00	4
13	Ag	0.00	0.10 t	0.1-0.86 t	0.55-1.00 t	0.55-1.00 t	4
14	Sn(II)	0.83	1.00	1.00	1.00	1.00	1
15	Pb	0.40	0.60	0.60	0.64	0.65	4
16	As(III)	0.54	0.78	1.00			5
17	Sb	0.90	1.00	1.00	1.00	1.00	1,5
18	Bi	0.80	1.00	0.92	0.85	0.78	4
19	Cr	0.03	0.06	0.09	0.23	0.30	1
20	Al	0.06	0.16	0.23	0.36	0.40	1
21	Fe(III)	0.11	0.58	1.00	1.00	1.00	4,7
22	Ni	0.07	0.13	0.20	0.32	0.33	4
23	Co	0.06	0.14	0.24	0.38	0.55	4
24	Rh	0.59	0.94	1.00	1.00	1.00	1,5
25	Pd	0.58	0.93	1.00	1.00	1.00	5,6
26	Pt	0.20 t	0.95	1.00	1.00 t	1.00 t	5,6
27	Au	0.67	0.97	1.00	1.00	1.00	6
28	Mn(II)	0.09	0.19	0.25	0.32	0.33	1
29	Sc	0.02	0.08	0.15	0.30	0.38	1
30	Y	0.02	0.07	0.13	0.24	0.30	1
31	La	0.00	0.03	0.08	0.17	0.24	1
32	Ti	0.07	0.19	0.26	0.43	0.49	1,7
33	V	0.12	0.20	0.27	0.43	0.47	1
34	Zr	0.00	0.01	0.03	0.11	0.14	1,7
35	Th	0.00	0.03	0.09	0.15	0.18	1
36	U(VI)	0.11	0.21	0.30	0.43	0.47	8
37	U(IV)	0.00	0.02	0.06	0.17	0.25	8
38	Ga	0.04	0.10	0.26	0.65	0.62	1
39	In	0.78	1.00	1.00	1.00	1.00	1
40	Tl(III)	0.93	1.00	1.00	1.00	1.00	1
41	Ce(III)	0.02	0.04	0.08	0.15	0.23	1
42	$B_4O_7^{-2}$	0.60	0.74	0.77	0.80	0.83	7
43	$Cr_2O_7^{-2}$	0.11 t	0.17	0.22	0.36	0.40	1
44	SeO_3^{-2}	0.63	0.78	1.00	1.00	1.00	10
45	TeO_3^{-2}	0.18	0.91	1.00	1.00	1.00	10
46	MoO_4^{-2}	0.21	0.38	0.48	0.53	0.55	7,8,9
47	PO_4^{-3}	0.53	0.82	0.90	0.96	0.96	16
48	ReO_4^-	0.64	0.94	1.00	1.00	1.00	9
49	WO_4^{-2}	0.00	0.00	0.00	0.00	0.00	9,10
50	$[Fe(CN)_6]^{-4}$	0.64	1.00	1.00	1.00	1.00	11,15
51	$[Fe(CN)_6]^{-3}$	0.52 t	0.91				12
52	I^-	0.68	0.99	1.00	1.00	1.00	13
53	ClO_3^-	0.62	0.98	1.00	1.00	1.00	14

Method and/or reagents for detection

1 ammoniacal solution of 8-hydroxyquinoline in ethanol
2 aqueous solution of sodium cobaltinitrite
3 aqueous solution of sodium rhodizonate
4 aqueous solution of yellow ammonium sulfide
5 gaseous hydrogen sulfide
6 the test with thallium nitrate and stannous chloride[8] was modified: the chromatogram is first sprayed with thallium nitrate solution and immediately after with stannous chloride. Gold and palladium form a brown-grey stain and platinum an orange-brown one
7 saturated solution of curcuma in ethanol[9]
8 aqueous solution of potassium ferrocyanide
9 hydrochloric acid solution of ammonium thiocyanate and stannous chloride
10 hydrochloric acid solution of stannous chloride
11 aqueous solution of uranyl acetate
12 freshly prepared aqueous solution of ferrous sulphate
13 the spot of iodide on the developed chromatogram is itself yellow-brown coloured
14 the test with manganous sulphate and phosphoric acid[10] was modified: a mixture of both was sprayed on the dried chromatogram giving a violet coloration of the chlorate spot
15 aqueous solution of ferric sulphate
16 aqueous solution of ammonium molybdate and stannous chloride

Detection of spots. The reagents and techniques are shown in Table I. No satisfactory reagent was found for potassium, rubidium, caesium and arsenic for highly acid media.

RESULTS

Table I shows the R_F values obtained. Some artificial mixtures were separated in one or two dimensions as shown in Fig. 2.

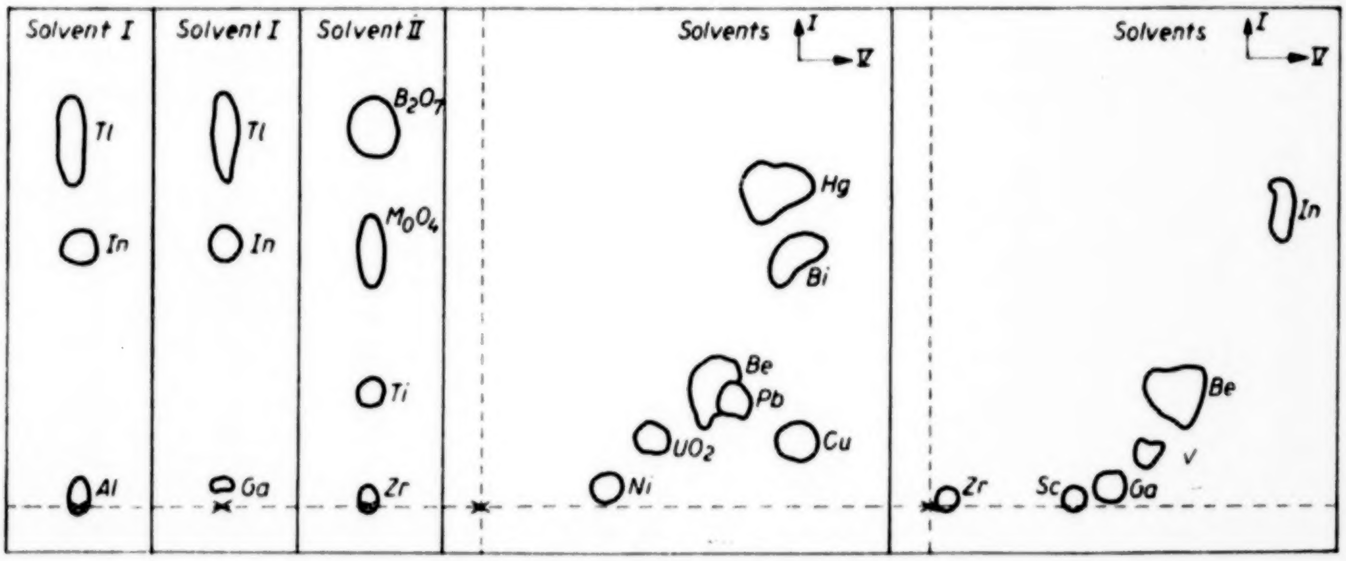

Fig. 2.
Some one and two dimensional separations of ions.

ACKNOWLEDGEMENT

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SUMMARY

The R_F values of fifty four inorganic ions were measured in mixtures of butanol and hydrobromic acid. In comparison with similar butanol-hydrochloric acid mixtures Cu, Pb, Te, Rh and In are better extracted in these mixtures (higher R_F values). This is in agreement with solvent extraction equilibrium data. Numerous separations are possible.

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RÉSUMÉ

Les valeurs de R_F de cinquante-quatre ions inorganiques ont été déterminées dans des mélanges butanol-acide bromhydrique. Pour les éléments suivants: Cu, Pb, Te, Rh et In, l'extraction est meilleure qu'avec des mélanges semblables butanol-acide chlorhydrique (valeurs de R_F plus élevées), ce qui correspond aux données obtenues en étudiant les équilibres d'extraction par les solvants. De nombreuses séparations sont possibles.

ZUSAMMENFASSUNG

Die R_F-Werte von 54 anorganischen Ionen wurden in Gemischen von Butanol und Bromwasserstoffsäure gemessen. Im Vergleich zu ähnlichen Gemischen von Butanol und Salzsäure werden durch Bromwasserstoffsäuregemische Cu, Pb, Te, Rh und In besser extrahiert (höhere R_F-Werte), was mit den durch Bestimmung der Lösungsmittelextraktions-Gleichgewichte erhaltenen Resultaten übereinstimmt. Viele Trennungen sind möglich.

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ELECTROCHROMATOGRAPHY IN THE SEPARATION OF IONS

by

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Electrochromatography aids in the detection and isolation of ions both organic and inorganic. Conditions of ions in solutions can be ascertained from the migration sequences and direction of migration. Relative migration rates and the reversal of the direction of migration due to complex formation sometimes serve the complete or absolute separation of certain ions, cations or anions, from their mixtures. Analytical separations and identifications based on electrical migration are thus possible. Change of electrolyte or its concentration is found at times to be very helpful for the purpose[1-7].

This paper deals with the electrochromatographic migration rates of individual inorganic ions, such as, Cu, Cd, Pb, Bi, Co and Ni and their separation from each other with very common types of electrolytes of different strengths. The electrolytes are: hydrochloric acid, potassium chloride, ammonium chloride, potassium iodide, ammonium thiocyanate, sodium nitrite, ammonium hydroxide, potassium cyanide, potassium cyanide just acidified with glacial acetic acid, tartaric acid, sodium potassium tartrate, sodium potassium tartrate made ammoniacal, citric acid, sodium citrate, acetic acid, sodium salt of EDTA and sodium salt of EDTA made ammoniacal.

Cations of the binary mixtures of the type Ni-Bi, Ni-Co, Ni-Cu, Co-Pb, Co-Bi, Ni-Pb, Co-Cu and Cu-Bi have been separated with *N* tartaric acid. Similar separations of Ni-Cu, Ni-Cd, and Co-Cu with 0.1*N* citric acid, Ni-Cu, Cu-Cd and Co-Cu with 0.1 *N* tartaric acid, Ni-Co with *N* potassium cyanide acidified with acetic acid, Co-Bi with 0.1*N* potassium chloride, Ni-Cd, Ni-Pb, Co-Cu and Cu-Pb with 0.1*N* sodium citrate, Pb-Bi with 0.1*N* hydrochloric acid, Cu-Bi and Pb-Bi with 0.1*N* sodium salt of EDTA, Cu-Cd with 0.1*N* potassium cyanide and with 0.1*N* sodium potassium tartrate and Ni-Bi with 0.1*N* ammonium thiocyanate have been achieved.

It has been observed that the ions of Co and Cu in 0.1*N* sodium citrate medium migrate towards the anode whereas in *N* tartaric acid both migrate towards the cathode, in 0.1*N* sodium citrate, Ni and Cd are anionic whereas in 0.1*N* citric acid both of them are cationic. Again Pb and Ni are anionic in 0.1*N* sodium citrate but cationic in *N* tartaric acid.

Cations of ternary mixtures, such as of Ni-Pb-Bi and Co-Pb-Bi with 0.1*N* sodium nitrite, Cd-Pb-Bi with *N* tartaric acid, Ni-Cd-Bi, Co-Cd-Bi and Cu-Cd-Bi with 0.1*N* hydrochloric acid, Ni-Cd-Bi, Cu-Cd-Bi and Cu-Pb-Bi with 0.1*N* potassium chloride and Co-Cd-Bi with 0.1*N* ammonium chloride, have been separated.

With 0.1*N* ammonium thiocyanate, cations from quaternary mixtures of the types Cu-Cd-Pb-Bi, Co-Cd-Pb-Bi, Ni-Cu-Pb-Cd and Co-Cu-Pb-Cd can easily be separated from each other and similarly with 0.1*N* ammonium chloride, Cu-Cd-Pb-Bi and with 0.1*N* potassium iodide, Co-Cd-Pb-Bi and Ni-Cd-Pb-Bi can be separated from each other.

Apparatus and experimental procedure

Several forms of electromigration apparatus based on the principle of DURRUM are available or may be constructed to suit particular investigation. Ours is the simplest form of apparatus. It consists of one d.c. ammeter, one d.c. voltmeter, a sliding rheostat, two platinum electrodes, two small glass tumblers, a plastic sheet with two straight slits and two small round holes for fixing electrodes to cover the two small glass tumblers containing electrolytes, an inverted T shaped plastic stand to be placed in the middle of the plastic sheet in between the two slits, a cover to enclose the set and Whatman filter paper No. 2, cut into strips of size 44 cm × 1 cm.

The filter paper strip is placed on the inverted T shaped stand while its two ends pass through the slits and touch the electrolyte in the two glass tumblers. Electrodes are introduced into the two glass tumblers through the holes. The top region *i.e.*, the centre of the paper strip is marked with a pencil. One drop, 0.01 ml, of the mixture of nitrates of the cations is placed on the starting point (1 ml of each solution having a cation concentration of 4.5 mg/ml is mixed for the preparation of the mixtures). The paper strip is moistened carefully with the electrolyte. The strip is then covered and electrodes are connected to a source of d.c. current at a potential of 150 V. In cases of binary and ternary mixtures, the current has been passed for 5 h, for quaternary mixtures, for 10 h and for pentanary mixtures, it has been passed for 12 h. After the experiment, the strip of paper is taken out, air dried and the zones of the separated ions are then located by spraying the paper with proper developing agent.

Separation sequences of ions are given in Tables I and II.

TABLE I

Binary mixture	*Ternary mixture*	*Quaternary mixture*	*Electrolytic soln.*
—Ni,Bi:; —Co,Ni:; —Ni,Cu:; —Co,Pb:; —Co,Bi:; —Ni,Pb:; —Co,Cu:; —Cu,Bi:;	—Cd,Pb,Bi:		*N* tartaric acid
—Ni,Cu:; —Cd,Cu:; —Co,Cu:			0.1 *N* tartaric acid
—(Cd):Cu^{+}			0.1 *N* sodium potassium tartrate
—Ni,Cu:; —Cd,Ni:; —Co,Cu:			0.1 *N* citric acid
:Cd,Ni^{+};:Pb,Ni^{+}; :Co,Cu^{+};:Pb,Cu^{+}			0.1 *N* sodium citrate
:(Bi),Cu^{+};:Bi,Pb^{+}			0.1 *N* sodium salt of EDTA
:Bi, Pb^{+}			0.1 *N* sodium salt of EDTA made ammoniacal
:Cd,Cu^{+}			0.1 *N* potassium cyanide
—Co:Ni^{+}			*N* potassium cyanide acidified with acetic acid
	—Ni,Pb:(Bi)$^{+}$; —Co,Pb:(Bi)$^{+}$;		0.1 *N* sodium nitrite
—Pb:Bi^{+}	—Ni:(Cd),Bi^{+}; —Co,(Cd):Bi^{+}; —Cu:(Cd),Bi^{+}		0.1 *N* hydrochloric acid
—Co:(Bi)$^{+}$	—Ni,Cd:Bi^{+}; —Cu,Cd,Bi:; —Cu,Pb,Bi:		0.1 *N* potassium chloride
		—Co:Pb,Bi,Cd^{+}; —Ni:Pb,Bi,Cd^{+}	0.1 *N* potassium iodide
	—Co,Cd,Bi: —Ni,Cd,Bi:	—Cu,Pb,Cd:Bi^{+}	0.1 *N* ammonium chloride
—Ni:(Bi)$^{+}$		—Pb,Cd,Cu:Bi^{+}; —Pb,Co,Cd,Bi:; —Pb,Co,Cd:Cu^{+}; —Pb,Ni,Cd:Cu^{+}	0.1 *N* ammonium thiocyanate

In the tables, the electrodes are indicated by the signs + and — and the starting point by :. When the movements of the ions are directed towards the cathode, they are shown on the left side of the starting point, while when they are directed towards the anode they are shown on the right side of the starting point. An ion which moves partly towards the cathode and partly towards the anode is included in parentheses.

In Table II are given the results for some mixtures whose cations cannot be completely separated but can easily be identified. The ions included within the sign [ ] indicate that a portion of their migration zones is common.

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TABLE II

Ternary mixture	*Quaternary mixture*	*Pentanary mixture*	*Electrolytic soln.*
	—Ni:[(Cu),Cd],Bi^{+}		0.1 *N* hydrochloric acid
:[Pb,Co,Cu] —[Co,Cu]:(Bi)			0.1 *N* sodium citrate
:[Pb,Ni,Cu]			0.1 *N* ammonium chloride
	—[Cu,Ni,Cd],Bi:	—Pb,[Co,Cd,Cu:(Bi)]	0.1 *N* ammonium thiocyanate
—[Cd,Ni],Cu:	—[Co,Ni,Pb],Bi: —[Co,Ni],Cu,(Bi): —[Co,Ni,Pb,Cu]:		*N* tartaric acid

SUMMARY

Electrochromatography has been utilized for the study of the separation of ions and their rate of migration in electrolytes of different strengths. Ions of quaternary mixtures, as Cu-Cd-Pb-Bi, Co-Cd-Pb-Bi, Ni-Cu-Pb-Cd, Co-Cu-Pb-Cd and Ni-Cd-Pb-Bi, have been effectively separated from each other on a 1 cm-filter paper (Whatman No. 2) strip at 150 V. Cations of pentanary mixtures of the type Pb-Co-Cd-Cu-Bi, though failed to give complete separation zones, could be easily indentified. Several binary and ternary mixtures of cations have also been separated with distinct separation zones.

RÉSUMÉ

Les auteurs ont étudié par électrochromatographie une méthode de séparation d'ions et ils ont déterminé leur vitesse de migration dans des électrolytes de différentes concentrations. Des ions de mélanges quaternaires tels que Cu-Cd-Pb-Bi, Co-Cd-Pb-Bi, Ni-Cu-Pb-Cd, Co-Cu-Pb-Cd et Ni-Cd-Pb-Bi ont pu être séparés les uns des autres sur une bande de papier filtre de 1 cm (Whatman No. 2) à 150 volts. Pour des mélanges de 5 cations du type Pb-Co-Cd-Cu-Bi, on n'obtient pas des zones de séparation très distinctes, mais l'identification de ces ions est facile. On est arrivé également à séparer en zones distinctes des cations de plusieurs mélanges binaires ou ternaires.

ZUSAMMENFASSUNG

Mit Hilfe der elektrochromatographischen Methode wurde die Trennung von Ionen und ihre Wanderungsgeschwindigkeit in Elektrolyten verschiedener Stärke untersucht. Ionen von vierfachen Gemischen, wie Cu-Cd-Pb-Bi, Co-Cd-Pb-Bi, Ni-Cu-Pb-Cd, Co-Cu-Pb-Cd und Ni-Cd-Pb-Bi konnten auf 1 cm Filterpapierstreifen (Whatman No. 2) bei 150 V gut von einander getrennt werden. Die Kationen von fünffachen Gemischen wie Pb-Co-Cd-Cu-Bi ergaben zwar keine vollständig getrennten Zonen, konnten aber leicht identifiziert werden. Für die Kationen verschiedener zweifacher und dreifacher Gemische konnten deutlich getrennte Zonen erhalten werden.

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THE DETERMINATION OF PHENOLS BY CHROMATOGRAPHY AND SPECTROPHOTOMETRY OF THEIR METHYL ETHERS

II. THE SEPARATION AND QUANTITATIVE DETERMINATION OF METHYL ARYL ETHERS

by

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In part I of this series[1], the determination of the ultraviolet absorption spectra in cyclohexane solution of a number of methyl aryl ethers was described. These compounds, by virtue of their characteristic spectra may be readily recognized, and if present together, may be separated by elution chromatography on suitable alumina columns[2].

Preparation of materials

The alumina (Type H, 100-200 mesh, Peter Spence and Co. Ltd.) was deactivated by adding water in small amounts to a freshly opened cannister and shaking vigorously. For monomethoxybenzenes about 1 per cent of water was necessary; 2 per cent was better for monomethoxynaphthalenes whereas 5 per cent was appropriate for the dimethoxybenzenes.

The method of standardization of alumina for polycyclic hydrocarbons recently published[3] will give suitable material for this work. The cyclohexane and the pure methyl aryl ethers were prepared as described in part I of this series of papers.

Analytical procedure

The hydroxy compounds up to 5 mg in amount in cyclohexane solution (to 2 ml volume) were run into the methylation apparatus (Fig. 1), the solution was washed down with a little cyclohexane, and a few drops of dimethyl sulphate and of $2N$ sodium hydroxide coloured with methyl red were then added and the whole heated in a boiling water bath. The aqueous layer became red in a few minutes when more sodium hydroxide solution was added. A small globule of methyl sulphate was always kept at the bottom of the flask and the addition of both reagents continued as necessary throughout the methylation time (15 to 40 minutes according to the phenols present). Most phenols were quantitatively methylated in 15 minutes, but *p*-cresol, 2:4-xylenol, 3:4-xylenol, 3:5-xylenol, catechol, resorcinol and 2-naphthol required longer. All except catechol and resorcinol are completely converted in 40 minutes. Longer periods were necessary in all cases where larger quantities of phenols were present in greater volume.

After methylation the reaction vessel was cooled and the contents transferred to a small stoppered separating funnel where they were shaken vigo-

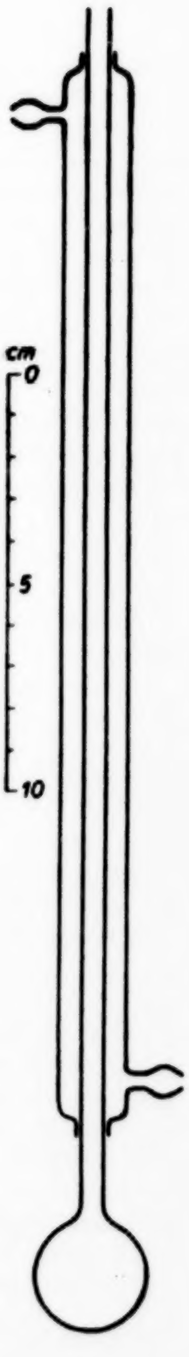

Fig. 1. Methylation apparatus. The bulb size may be increased for larger samples; normally it is of approximately 5 ml capacity.

rously with 30% sodium hydroxide to destroy the excess of methyl sulphate. The cyclohexane solution, if not more than 2 ml, was transferred to the chromatographic column; if greater than 2 ml it was evaporated to this bulk by drawing air through it at room temperature.

Chromatographic separation technique

Columns were prepared in pyrex glass tubes 1 cm in diameter and up to 30 cm long. The activated alumina, in depth up to 10 cm was introduced as a slurry in cyclohexane upon a glass wool plug closing the lower end of the column. While the solid was settling, the tube was gently tapped to ensure an evenly packed adsorbent. The solution of methyl aryl ethers in small volume (about ½ ml) were introduced on the top of the column, by means of a pipette as soon as the solvent had entered the column. Additional quantities of solvent (not more than 1 ml at a time) were then added in order to obtain even separations. Eluates were collected in approximately 3 ml fractions and when five of these had been collected, larger quantities of solvent could be added above the alumina to increase the rate of development.

Separation could be stopped for a while by corking the top of the column and immersing the bottom end in a tube of solvent. The cork was provided with a tap which was closed only when the cork was in position to avoid disturbing the packing of the column.

Successive eluates were examined in the Unicam S.P. 500 spectrophotometer in 1 cm quartz cells with a constant slit width of 0.3 mm, and the characteristic peak heights measured. The quantities of each compound were determined in each fraction by reference to standard optical heights.

Standardization

For the purpose of quantitative work a convenient absorption peak of longer wavelength was employed because general light absorption is less at long wavelengths. The method was standardized by recording the "standard optical height," (the peak height expressed in terms of the optical density scale of the S.P. 500 spectrophotometer at fixed slit width of 0.3 mm for a solution containing one microgram of substance in each ml of solution) of these absorption peaks. In order to measure the height an arbitrary choice was made. The wavelength distance between the previous minimum to the maximum was measured and the absorption of a point at equal distance in wavelength on the other side of the maximum was read. The mean of the absorption readings at this point and the minimum was calculated and subtracted from the absorption of the maximum. This was called the optical height of the peak and the standard optical height was obtained by dividing this by the concentration of the solution expressed in µg per ml. In Table I the standard optical heights for a number of methyl aryl ethers are tabulated.

TABLE I

STANDARD OPTICAL HEIGHTS FOR METHYL ARYL ETHERS IN CYCLOHEXANE SOLUTION

Compound	*Wavelength range (mµ)*	*Standard optical height (at 0.3 mm slit)*
Guaiacol	279.5-281.8-284.0	0.0094
Anisole	263.0-265.0-267.0	0.00195
	275.5-278.0-280.5	0.0122
o-Cresyl methyl ether	275.8-278.2-280.5	0.0054
m-Cresyl methyl ether	277.2-279.7-282.0	0.0075
p-Cresyl methyl ether	283.5-286.0-288.5	0.0088
2:3-Xylenyl methyl ether	277.0-279.0-281.0	0.0050
2:4-Xylenyl methyl ether	283.0-285.4-288.0	0.0045
2:5-Xylenyl methyl ether	279.0-281.4-284.0	0.0051
2:6-Xylenyl methyl ether	271.2-273.0-275.0	0.00044
3:4-Xylenyl methyl ether	282.5-284.7-287.0	0.00308
3:5-Xylenyl methyl ether	278.5-281.0-283.5	0.0055
o-Dimethoxybenzene	281.5-283.0-284.5	0.00206
m-Dimethoxybenzene	278.0-280.2-282.0	0.0052
p-Dimethoxybenzene	298.0-300.0-302.0	0.00270
1-Naphthyl methyl ether	317.5-320.0-322.5	0.0084
2-Naphthyl methyl ether	324.5-327.6-330.5	0.0113

Separation of mixtures of ethers

In order to test the method a number of mixtures of pure ethers were prepared in cyclohexane solution and separated on alumina columns 10 cm long as described above. The eluates were collected in tubes calibrated at 2.7 ml and the ethers present determined by measuring the peak heights of the absorption spectra. Fig. 2, which with its caption is self-explanatory, shows the separations so effected for a number of mixtures containing 100 μg of each compound.

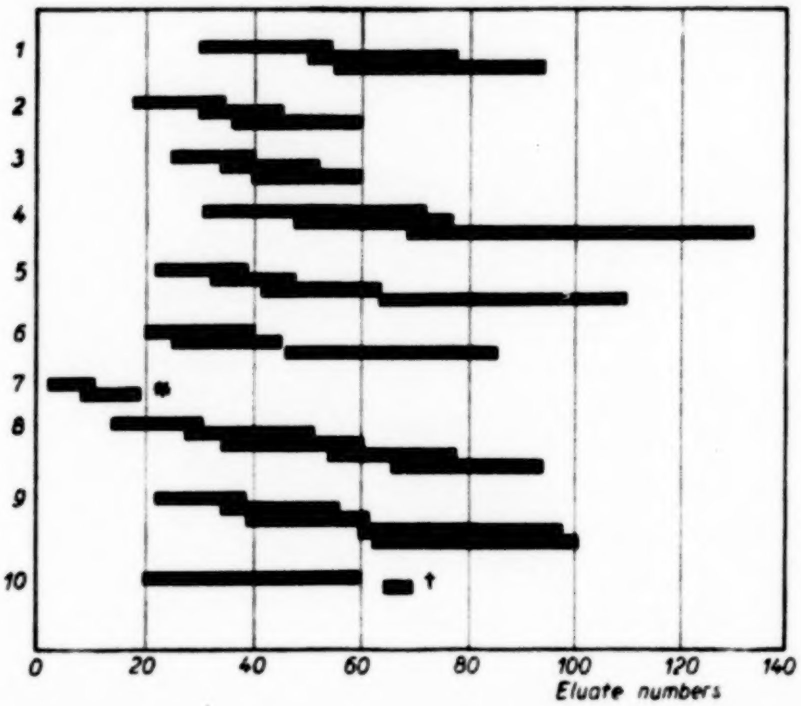

Fig. 2. Separation of mixtures of 100 μg quantities of aryl methyl ethers on alumina columns by elution with cyclohexane. The 2:4-xylenyl and 3:4-xylenyl ethers cannot be separated except on very short (2.5 cm) columns.* The 2-naphthyl ether does not elute with cyclohexane but is completely removed in 5 fractions with benzene.† 1. phenyl, *m*-cresyl, *p*-cresyl. 2. *o*-cresyl, 2:4-xylenyl, phenyl. 3. *p*-cresyl, 2:5-xylenyl, 2:4-xylenyl. 4. *p*-cresyl, 3:5-xylenyl, 1-naphthyl. 5. *o*-cresyl, 2:4-xylenyl, phenyl, *p*-cresyl. 6. 2:5-xylenyl, 2:4 and 3:4-xylenyl, 3:5 xylenyl. 7. 2:4-xylenyl, 3:4 xylenyl. 8. *o*-cresyl, 2:4 xylenyl, phenyl, *m*-cresyl, *p*-cresyl. 9. *o*-cresyl, 2:4-xylenyl, phenyl, *m*-cresyl, *p*-cresyl. 10. 1-naphthyl, 2-naphthyl.

It is generally found that the longer the column of alumina the more complete is the separation but with longer columns the eluates are more dilute and are therefore more difficult to analyse. The partial separation of the aryl methyl ethers does not necessarily preclude accurate determination, for, provided the two ethers separating together have distinctive absorption bands, each may be determined by the height of its characteristic absorption peaks.

The overall accuracy of the method depends upon the phenols being determined and their relative proportions; it is usually within 5 per cent and sometimes with simpler mixtures to within 2 per cent.

The Authors wish to acknowledge a grant from Imperial Chemical Industries Ltd., used in part to purchase chemicals.

SUMMARY

In this, the second of a series of papers on the determination of phenols by chromatography and spectrophotometry of their methyl ethers, details are given for the quantitative methylation of phenols in microgram amounts and their separation by elution with cyclohexane. The amounts of the separated methyl aryl ethers are determined by ultra-violet spectrophotometry.

RÉSUMÉ

Dans ce deuxième article d'une série de travaux sur le dosage les phénols par chromatographie et spectrophotométrie de leurs éthers méthylés, les détails sont donnés pour une méthylation quantitative des phénols à l'échelle microchimique, et pour une séparation par élution au moyen du cyclohexane. Les teneurs en méthylaryléthers, ainsi séparés, sont déterminées par spectrophotométrie dans l'ultra-violet.

ZUSAMMENFASSUNG

In dieser zweiten Arbeit in einer Reihe von Artikeln über die Bestimmung der Phenole durch Chromatographie und Spektrophotometrie ihrer Methyläther, werden Einzelheiten über die quantitative Methylierung von Phenolen in Mengen von der Ordnung des Mikrogramms und über ihre Trennung durch Elution mit Cyclohexan gegeben. Die Mengen der so getrennten Methylaryläther wurden durch Ultraviolett-Spektrophotometrie ermittelt.

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THE DETERMINATION OF PHENOLS BY CHROMATOGRAPHY AND SPECTROPHOTOMETRY OF THEIR METHYL ETHERS

III. THE DETERMINATION OF PHENOLS IN WOOD SMOKE

by

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Although very many studies have been made on the chemical composition of the products of destructive distillation of wood of various kinds, there has been little published on the composition of wood smoke. It may be assumed that many of the well-known constituents of the destructive distillation of wood are also present in wood smoke and a number of these have been detected and determined.

The most complete studies yet described are those of PETTET and his co-workers[1,2,3], who examined oak smoke obtained in an experimental plant designed to collect as much as possible of the products. Of these products the phenols are those in great measure responsible for the decay arresting properties and the desirable smell and taste imparted to smoked foods. Considerable interest therefore is attached to the determination of phenols in wood smoke.

Previous workers have reported the presence of phenol[3], cresols[4], guaiacol[4], catechol[5], 1-methylpyrogallol[10], 2,3-dihydroxy-5-methylanisole[10], 2,3-dihydroxy-5-ethylanisole[10], and 1,3-dimethylpyrogallol[5] in wood smoke, but most analytical results on smoke and smoked foods have been reported as "phenols" and calculated as phenol (C_6H_5OH)[4,6].

ANALYTICAL PROCEDURE

All reagents and materials were prepared as described in earlier papers in this series[7,8].

The wood smoke, obtained from the Torry Research Station, was made in a specially designed plant[9] producing smoke for curing fish and was trapped at —80°C and dissolved in ethyl alcohol. Fifteen ml of this alcoholic solution was mixed with 5 ml water and 20 ml chloroform and shaken vigorously. The chloroform layer was removed and the aqueous portion repeatedly extracted with chloroform containing 5 per cent of ethyl alcohol. The combined chloroform solutions were then extracted 8 times with 2*N* sodium hydroxide and methylated by heating under reflux with dimethyl sulphate for three hours. The methylated phenols were extracted with cyclohexane and made up to 15 ml.

The cresols and phenol were determined by taking 5 ml and separating on a column 11 cm long of alumina containing 1 per cent of added water. After about 60 ml of cyclohexane had passed, *o*-cresyl methyl ether appeared and was followed by the phenyl, *m*-cresyl and the *p*-cresyl ethers. When benzene was added to elute the last traces of the *p*-ether, some 1-naphthyl methyl ether was also detected.

The dihydroxybenzenes were determined as their ethers in 5 ml on a column of 2.5 cm of alumina containing 5 per cent of added water. The *m*- and *p*-dimethyoxybenzenes appeared first and were followed by the *o*-dimethoxybenzene.

The naphthyl ethers were determined by a second separation of the dimethoxybenzenes on a similar column.

The spectrophotometric techniques employed were exactly as previously described[8], and the results are shown in Table I.

TABLE I

PHENOLS PRESENT IN WOOD SMOKE

Phenol	*Amount* *micrograms in 1 ml original solution*
Phenol	22.1
o-Cresol	11.9
m-Cresol	22.6
p-Cresol	25.4
1-Naphthol	1.5
2-Naphthol	0.78
Catechol	179.0
Resorcinol	8.4
Quinol	10.3

Note: The monomethyl ethers of the dihydroxybenzenes, if present, are included in the amounts of dihydroxybenzenes. Guaiacol is known to be present and a new method for determining it in the presence of catechol is under investigation.

According to SHEWAN[4] the quantity of phenols calculated as C_6H_5OH in kippered herring is 15.2 mg/100 g. If, therefore, uniform absorption of all the phenols present in the smoke occurs during the curing process it may be assumed that the quantities in Table I represent the amounts in approximately 2 g of smoked fish.

ACKNOWLEDGEMENT

The authors wish to acknowledge a grant from Imperial Chemical Industries, Ltd., used in part to purchase chemicals and a gift of oak smoke condensate from the Torry Research Station, Department of Scientific and Industrial Research.

SUMMARY

The method previously developed for the determination of phenols by chromatography and spectrophotometry of their methyl ethers has been applied to their determination in wood smoke. Phenol, *o*-cresol, *m*-cresol, *p*-cresol, 1-naphthol, 2-naphthol and the three isomeric dihydroxybenzenes have all been determined in microgram amounts. Guaiacol, and possibly other methyl ethers of the phenols are also present.

RÉSUMÉ

La méthode, décrite précédemment pour le dosage des phénols par chromatographie et spectrophotométrie de leurs éthers méthyliques, a été appliquée au dosage de ces composés dans la fumée de bois. Phénol, *o*-crésol, *m*-crésol, *p*-crésol, 1-naphtol, 2-naphtol et les trois isomères du dihydroxybenzène ont pu être dosés à l'échelle microchimique. Le gaïacol et peut-être d'autres éthers méthyliques des phénols sont également présents.

ZUSAMMENFASSUNG

Die früher entwickelte Methode zur Bestimmung von Phenolen durch Chromatographie und Spektrophotometrie ihrer Methyläther wurde zur Bestimmung dieser Verbindungen im Holzrauche angewendet. Phenol, *o*-, *m*- und *p*-Kresol, 1- und 2-Naphtol und die drei isomeren Dihydroxybenzole wurden in Mengen von der Ordnung des Mikrogramms bestimmt. Guajakol und möglicherweise auch andere Methyläther der Phenole sind ebenfalls gegenwärtig.

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THE DETERMINATION OF PHENOLS BY CHROMATOGRAPHY AND SPECTROPHOTOMETRY OF THEIR METHYL ETHERS

IV. THE DETERMINATION OF PHENOLS IN CIGARETTE SMOKE

by

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The method of analysis previously described[1,2,3,4], has now been applied to the determination of phenols in tobacco smoke. Other studies dating from 1931 have indicated the presence of phenol[5,6,7], *o*-cresol[7], *m*-cresol[7], catechol[5], guaiacol[5,7] and the classes of compounds grouped under the headings phenols[8,9,10,11,12,13], polyphenols[5], phenolic acids[14], and creosote[6], in tobacco smoke, but in view of the varied means of obtaining the smoke (in some cases by techniques most unlike normal human smoking) the results are not clearly defined. The most reliable determination of phenols in tobacco smoke was made by RAYBURN, HARLAN AND HANMER[7], who used a machine to simulate human smoking.

EXPERIMENTAL

Main stream cigarette smoke was obtained by smoking a well-known brand of virginia cigarettes sold in this country. The apparatus and conditions of smoking were as previously described[15,16]. The smoke from 50 cigarettes was drawn through pure ethyl alcohol in the absorption flasks and the whole apparatus washed out with ethyl alcohol when the experiment was over. The red alcoholic solution (100 ml) was mixed with 50 ml of chloroform and 10 ml of water. The chloroform layer was removed and the aqueous layer extracted several times with chloroform containing 5 per cent of ethyl alcohol. The combined chloroform solutions were then extracted eight times with 2*N* sodium hydroxide and the alkaline solution methylated by heating under reflux with dimethyl sulphate for three hours. The methylated phenols were then extracted with cyclohexane and made up to 10 ml. Aliquot portions were analysed by the method previously described[3].

TABLE I

PHENOLS PRESENT IN CIGARETTE SMOKE

Phenol	*Micrograms of phenol per cigarette*
Phenol	123
o-Cresol	22
m-Cresol	18
p-Cresol	40
1-Naphthol	0.27
2-Naphthol	0.54
o-Dihydroxybenzene	61
m-Dihydroxybenzene	8
p-Dihydroxybenzene	83

Note: The monomethyl ethers of the dihydroxybenzenes, if present, are counted as dihydroxybenzenes. Guaiacol is known to be present to approximately 6 per cent of the total phenols[7] and a new method is being developed for the determination of mono ethers in the presence of dihydroxybenzenes.

The cresols and phenol were determined by taking 0.4 ml of solution (equivalent to 2 cigarettes) and separating on a 10 cm column of alumina, containing one per cent of added water. The four ethers were separated from each other sufficiently well for a determination of each to be made.

The two naphthols were determined in 3 ml of solution (equivalent to 15 cigarettes) on a 7.5 column of alumina containing 5 per cent of added water. After 10 ml of cyclohexane had passed through the column, both naphthols could be detected. A further 10 ml was collected and re-chromatographed on a 14 cm column. The amounts of each ether were calculated in each fraction.

The dihydroxybenzenes were determined in 0.3 ml of solution (equivalent to 1.5 cigarettes) by use of a 5 cm column of the same type of alumina used for the naphthols. The chromatographic order was, *m*-dimethoxy, *p*-dimethoxy and *o*-dimethoxy; the first two were not completely separated but the last was obtained pure after 80 ml had passed through the column.

Spectrophotometric techniques were exactly as previously described, and the results, expressed as micrograms of the phenol in each cigarette are shown in Table I.

The results shown in Table I agree well with those of RAYBURN, HARLAN AND HANMER, who mention the presence of only phenol, *o*-cresol, *m*-cresol and guaiacol.

ACKNOWLEDGEMENT

The authors wish to acknowledge the support of the Medical Research Council, and also a grant from Imperial Chemical Industries, Ltd., used in part to purchase chemicals.

SUMMARY

In this, the fourth of a series of papers on the determination of phenols by chromatography and spectrophotometry of their methyl ethers, details are given for the determination of the phenols present in cigarette smoke. Phenol, *o*-cresol, *m*-cresol, *p*-cresol, 1-naphthol, 2-naphthol, and the three isomeric dihydroxybenzenes were found and determined. There is evidence that the latter are originally present in part as their monomethyl ethers and a method is under investigation to determine the proportions of the ethers present.

RÉSUMÉ

Dans cet article, le quatrième d'une série sur le dosage des phénols par chromatographie et spectrophotométrie de leurs éthers méthyliques, les détails sont donnés pour le dosage des phénols dans la fumée de cigarette. Les composés suivants: phénol, *o*-crésol, *m*-crésol, *p*-crésol, 1-naphtol, 2-naphtol et les trois isomères du dihydroxybenzène ont pu être décelés et dosés. Certains faits font penser que ces derniers sont originairement présents en partie sous forme d'éthers monométhyliques. Des recherches sont en cours pour établir une méthode de détermination des proportions des éthers présents.

ZUSAMMENFASSUNG

In dieser vierten Mitteilung in einer Reihe von Arbeiten über die Bestimmung der Phenole durch Chromatographie und Spektrophotometrie ihrer Methyläther, werden Einzelheiten über die Bestimmung der im Zigarettenrauch enthaltenen Phenole gegeben. Phenol, *o*-, *m*- und *p*-Kresol, 1- und 2-Naphtol sowie die drei isomeren Dihydroxybenzole wurden aufgefunden und bestimmt. Tatsachen weisen darauf hin, dass Letztere ursprünglich teilweise als Monomethyläther vorliegen. Eine Methode zur Bestimmung der Proportionen der vorhandenen Äther ist in Bearbeitung.

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VAPOUR PHASE CHROMATOGRAPHIC DETERMINATION OF BENZENE, NAPHTHALENE AND OTHER HYDROCARBONS IN WASH OIL

APPLICATION OF A SIMPLE AND ACCURATE DETECTION METHOD FOR VAPOUR PHASE CHROMATOGRAPHY

by

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INTRODUCTION

Vapour phase chromatography has proved to be a very valuable technique for analysis and identification of volatile substances in a wide variety of complex mixtures. Its principle and scope have already been discussed in numerous papers, *e.g.*[1,2,3,4,5]; therefore it suffices here to give a short description of the principal features.

The method is based on the phenomenon that, if a mixture of vaporized substances is introduced into a gas stream and led through a column containing a porous solid phase impregnated with a non-volatile solvent (stationary phase), a separation is effected because the differences in the Henry coefficients of the substances give rise to different rates of flow through the column. The separated components are detected at the end of the column; this is mostly done by means of an apparatus which measures the thermal conductivity of the effluent. Rapid changes in conductivity are registered by an automatic recorder and indicate that one of the components of the mixture is issuing from the column.

However, such an apparatus is rather expensive. Moreover, besides standardization with pure compounds this method of detection requires an accurate adjustment of

1. the gas velocity,
2. the temperature of the column and of the conductivity cell and
3. the composition of the carrier gas.

We therefore suggested a simpler technique[6] that may be used in any laboratory. It is based on combustion of the separated components over copper oxide (700°C) and immediate titration of the resulting carbon dioxide in pyridine solution with sodium methylate as a titrant.

The development of vapour phase chromatography has opened up new possibilities for the analysis of wash oil and similar complex mixtures.

This has enabled us to satisfy the need of a rapid method for estimating small amounts of *benzene in wash oil* (of the order of 100 mg per liter). The method, described below, is a combination of a kind of dynamic estimation of the vapour pressure and a vapour phase separation which makes it possible to determine the benzene content of the oil within an hour, using a simple apparatus. If required, toluene and xylene may be determined simultaneously with the benzene.

Secondly we were interested in a rapid and reliable method for estimating relatively large amounts of ***naphthalene in wash oil*** (0.5—30 %). Several methods have been developed for this purpose but these have the drawback of being rather time-consuming and not very accurate. Using the possibilities offered by vapour phase chromatography, we succeeded in designing a rapid and simple procedure consisting of a direct separation of the volatile oil components over a suitable column at 200°C. Here again other oil components such as methylnaphthalene, dimethylnaphthalene and those of lower boiling point, *e.g.* benzene, toluene, xylene, coumarone may be determined simultaneously.

The methods described below may also be used for determining benzene, naphthalene, *etc.* in gases. The components are first concentrated by condensation in a cooled receiver of special shape and subsequently separated on a chromatographic column.

EXPERIMENTAL

Benzene in wash oil

Considering that a method based on total expulsion of the benzene from the oil takes a lot of time, we resolved to choose another way.

A well-defined portion of the benzene is expelled by passing a stream of nitrogen at constant rate (0.6 l per hour) through the oil for fifteen minutes, at exactly 100°C, the compounds carried along by the gas stream being collected in a strongly cooled receiver (—40°C) of special shape. This receiver can be easily connected to a chromatographic column containing sterchamol impregnated with dinonylphthalate and heated up to 80°C. The mixture is carried through the column by means of a stream of gas and thus separated. The benzene fraction, issuing from the column is burnt over copper oxide (700°C) and titrated as carbon dioxide. The method is standardized against samples of wash oil with known and varying percentages of benzene, made up by addition of benzene to absolutely benzene-free oil.

The reproducibility of the method appears from the values compiled in Table I. These were found for an experimentally determined factor (*f*), that is to say the ratio between the number of milligrams of benzene per l wash oil and the amount of benzene (in mg) expelled in 15 minutes (see procedure).

TABLE I

REPRODUCIBILITY OF FACTOR *f*

Amount of benzene per litre wash oil, mg	*Amount of benzene expelled in 15 minutes, mg; temperature 100°C; gas rate 0.6 l per hour*	*Ratio f*
73	0.18	410
73	0.18	410
200	0.46	430
200	0.46	430
295	0.68	430
295	0.68	430
315	0.69	460
315	0.68	460
395	0.87	450
395	0.89	440
615	1.54	400
615	1.43	430

In addition, the accuracy of the method was checked as follows. Large amounts of samples (*e.g.* one litre), the benzene content of which was estimated by the method described above, were heated to 100°C after which the volatile components were expelled with a rapid stream of inert gas within 3 hours. The bulk of the naphthalene was removed from the gas stream by cooling; the other components were adsorbed on charcoal and subsequently removed by steam. Upon determination of the benzene content of the hydrocarbon layer by infrared analysis, the percentage in the original sample was calculated. The results obtained by both methods agree satisfactorily as appears from Table II.

The method was used in one of our works laboratories for over a year, without it being necessary to change the stationary phase in the separation column.

TABLE II

ANALYSIS OF WASH OIL SAMPLES

Sample No.	*Amount of benzene found, mg per litre*	
	Chromatographic method	*Infrared method*
1	55	45
2	210	190
3	35	30
4	175	170
5	60	55
6	1250	1125
7	45	40
8	290	230

Interferences

It is obvious that large amounts of volatile substances in the oil lead to erroneous results. In our experiments water proved to interfere seriously because the (undissolved) water evaporates very quickly, carrying along benzene in amounts depending on the volume of water vaporized. Therefore the oil was thoroughly dried before analysis by shaking with powdered calcium chloride.

In order to check if the "benzene" issuing from the partition column was pure C_6H_6, the combustion tube was removed, the fraction collected in a cooled receiver and examined by infrared analysis.

Only *one* other component was detected in this way, *viz.* thiophene, which was present in an amount equivalent to about 2% of the amount of benzene.

Determination of other volatile components

If it is desired to know also the toluene and xylene contents of the wash oil, these can be determined in exactly the same way, after testing with oil, containing known amounts of these compounds. In such cases it is recommendable to choose a somewhat higher column temperature ($\sim$ 100°C) in order to shorten the separation process.

Method

Materials used

1. Sodium methylate, in methanol 0.1 N (titre *t*), standardized with benzoic acid
2. Thymol blue, solid
3. Pyridine, water-free or acetone
4. Dinonyl phthalate
5. Sterchamol, particle size 0.4-0.6 mm
6. Oxygen } dried and CO_2-free
7. Nitrogen } dried and CO_2-free

References p. 566

Apparatus (see Fig. 1)

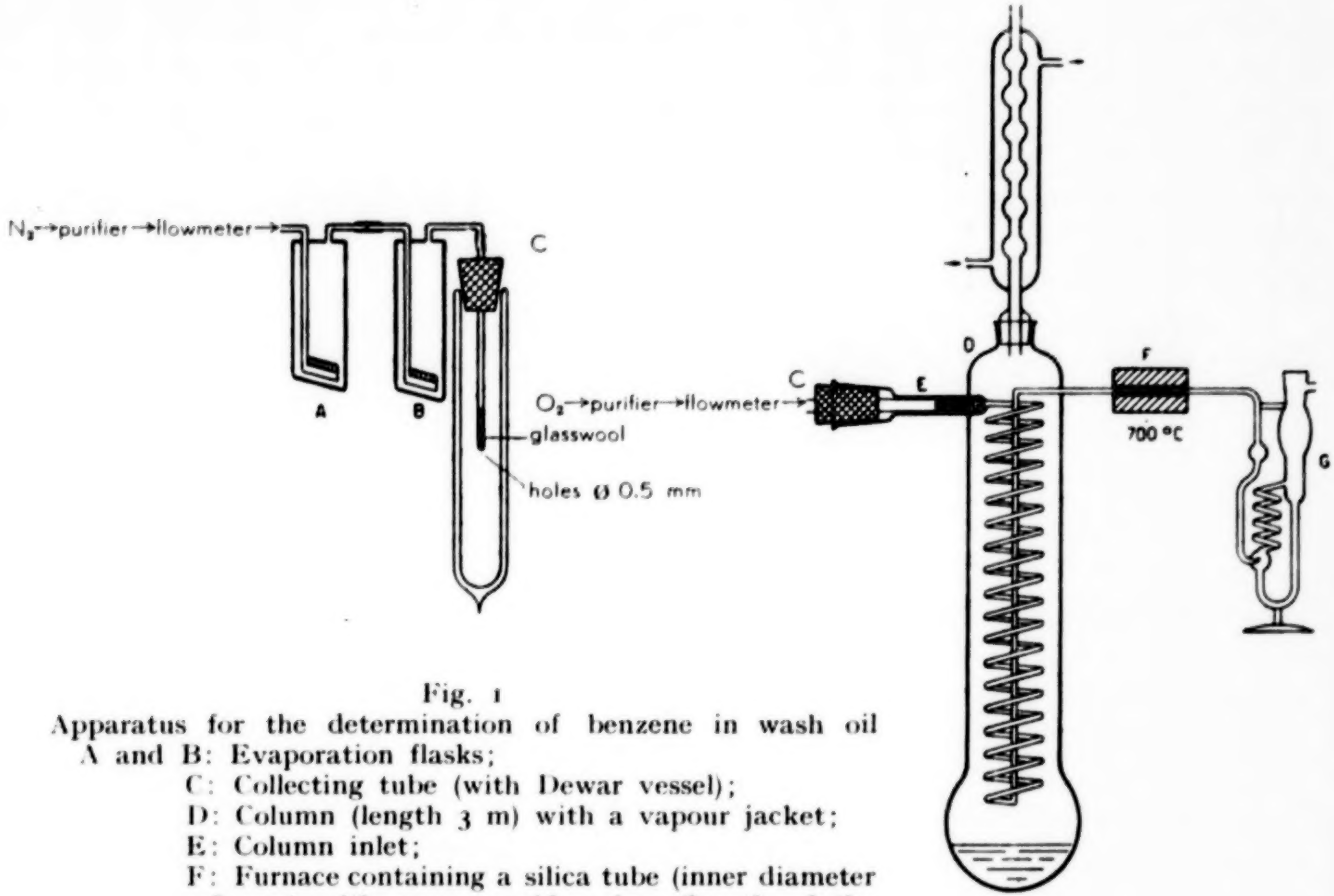

Fig. 1
Apparatus for the determination of benzene in wash oil
A and B: Evaporation flasks;
C: Collecting tube (with Dewar vessel);
D: Column (length 3 m) with a vapour jacket;
E: Column inlet;
F: Furnace containing a silica tube (inner diameter 7-8 mm) with copper oxide wires (length of the copper oxide layer 150 mm);
G: titration vessel.

Preparation of the apparatus

Dissolve 30 g of dinonyl phthalate in ether, add 100 g of sterchamol to the solution and evaporate the ether whilst stirring. Transfer the dry material into a suction flask, connect the narrow opening to the spiral tube, plug the opposite end of the tube with cotton wadding, slant the flask, and draw the material into the tube by suction.

Heat the column by means of boiling ethanol. Connect the furnace to the mains and keep the temperature at 700° C. Pass oxygen through the column until the amount of CO_2 issuing per unit time has become constant.

After that run a blank at an oxygen flow rate of 2.6 l per hour (consumption of sodium methylate per minute = v_0 ml).

Procedure

Shake vigorously about 150 ml wash oil with 25 g powdered $CaCl_2$ in a stoppered flask for about 10 minutes. Allow the $CaCl_2$ to settle. Add 50 ml wash oil into each evaporation flask and place the flasks in boiling water covered with a layer of paraffin oil. Lead nitrogen through the oil at the rate of 0.62 l/h for 5 min. Connect the collecting tube C with the outlet of flask B. Cool in liquid nitrogen and pass nitrogen through the wash oil for 15 minutes.

Meanwhile, connect the titrating vessel with furnace F, put in 10 ml pyridine or acetone, add about 2 mg indicator and neutralize with sodium methylate until the colour just turns blue.

After the nitrogen has been passed through for 15 minutes, remove tube C from the apparatus. Wipe the outer wall of the tube dry with a clean cloth, insert the tube into the column as shown in the figure and connect the oxygen supply line. All these manipulations are to be carried out as quickly as possible. Adjust the oxygen flow rate to 2.6 l/h, heat the column section containing tube

C with a small flame and simultaneously start the stop watch. Keep the pyridine or acetone solution neutral by addition of sodium methylate. After twenty minutes read the level of the burette and titrate the carbon dioxide formed up to and including the 45th minute (consumption v ml). Subsequently expel other compounds from the column (see remark 2).

Calculation

$$(v - 25\ v_0).t.13.f = \text{mg/l benzene}$$

where

$$f = 435, \text{ an experimentally determined factor (see remark 1).}$$

Remarks

1. A number of tests was carried out with benzene-free wash oil containing a known amount of benzene. Using the test results the above factor was calculated which gives the relationship between the amount of benzene expelled in 15 minutes and the amount of benzene present in 1 litre of wash oil.
2. To remove substances with higher boiling points than benzene rapidly from the column, air is led through the apparatus in the opposite direction at a rate of about 5 l/h.

Naphthalene in wash oil

The percentage of naphthalene in wash oil is much higher than that of benzene and therefore a previous concentration of this component is not necessary. The separation of naphthalene and higher boiling compounds involves the difficulty that a high column temperature must be used which makes high demands on the stability and non-volatility of the stationary phase. After some preliminary experiments, silicone grease (Dow-Corning Co.) was chosen for this purpose. Volatile components in the grease were removed by the method described by CROPPER *et al.*[7] after which it appeared to be very stable. A column filled with sterchamol impregnated with this grease has been in use for one year now and it still works very well, in spite of the fact that the temperature has been kept at 200°C. To separate naphthalene from other wash oil components it was found desirable to use a column of 6 m in length*. On account of the high temperature of the column the carrier gas had to be free from oxygen; therefore oxygen-free nitrogen was used. The oxygen needed for effecting complete combustion was introduced behind the partition column, care being taken that no oxygen could diffuse back. Furthermore the high temperature required, made it necessary to heat the column electrically. In order to prevent condensation of the naphthalene, the space between the end of the column and the combustion zone was kept as short as possible, care being taken, however, that the temperature of the stationary phase at the end of the column did not rise much above 200°C. A small zone of sterchamol, not impregnated with silicone proved to be very satisfactory.

Complete combustion of naphthalene and similar substances is rather difficult. Consequently it is desirable to use a copper oxide zone of 40 cm at 800°C, while the catalyst has to be of good quality. Now and then the method is checked with pure naphthalene or mixtures of naphthalene and methylnaphthalene, both to verify whether the combustion is complete and to determine the retention time.

Table III gives the results of analyses carried out with mixtures of known composition.

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* At the beginning of the experiment the column efficiency is such that a length of 6 m is somewhat high, but in the course of about two months the efficiency decreases.

TABLE III

ANALYSIS OF MIXTURES OF NAPHTHALENE AND METHYLNAPHTHALENE

Amount of sample mg	*Naphthalene mg*		*Methylnaphthalene mg*	
	Calc.	*Found*	*Calc.*	*Found*
5.40	0.51	0.46	4.89	4.48
9.44	0.90	0.89	8.54	8.33
4.01	3.47	3.48	0.54	0.55
6.74	5.83	5.75	0.91	0.85
6.74	2.65	2.52	4.09	3.94
5.68	2.23	2.20	3.45	3.49
6.59*	3.29	2.90	3.30	3.01

* Copper oxide aged.

The reproducibility of the method for wash oil samples is shown in Table IV.

TABLE IV

ANALYSIS OF WASH OIL SAMPLES

Sample No.	*Weight of sample mg*	*% naphthalene*	*% methylnaphthalene*
1	87.6	2.0	—
	89.2	1.8	—
2	2.6	24.9	—
	18.4	25.0	—
3	7.0	4.5	4.9
	26.0	4.6	4.8
4	12.5	7.5	4.7
	26.5	7.6	4.6
5	29.0	7.5	4.7
	13.7	7.9	4.6

The table shows that the reproducibility is very satisfactory, both for naphthalene and for methylnaphthalene.

To check whether other components issue from the column simultaneously with those mentioned above, the fractions were collected in a cooled receiver and examined by infrared analysis. The naphthalene fraction consisted of practically pure naphthalene whereas the methylnaphthalenes were contaminated with other compounds.

Method

Materials used

Sodium methylate in methanol 0.1 N (titre t), standardized with benzoic acid
Thymol blue, solid
Pyridine (water-free) or acetone
Silicone grease: "High vacuum grease, Dow Corning"
Sterchamol; particle size 0.4-0.6 mm
Nitrogen } free of water and carbon dioxide
Oxygen }

Sample

Use an amount of wash oil containing 1-6 mg of naphthalene.

References p. 566

Apparatus (see Fig. 2)

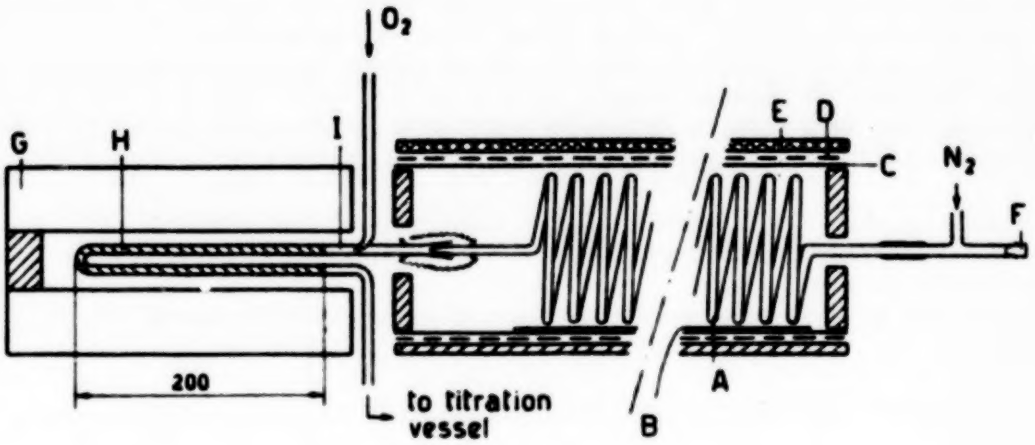

Fig. 2

Apparatus for the separation of naphthalene and methylnaphthalene

A: Column (pyrex) length 6 m, inner ø 6 mm, heated with Kanthal wire (D) and wrapped up in asbestos cord (E);
B: Glass rods to isolate the spiral column from the hot jacket;
C: Glass tube (pyrex), inner ø 45 mm;
D: Kanthal heating wire (2 × 0.1 mm, 7.5 Ω per m);
E: Asbestos cord; F: Rubber stopper; G: Furnace (800°C);
H: Silica tube filled with copper oxide, inner ø 6 mm; I: Oxygen inlet, inner ø 1 mm

Titration vessel
2 Flow meters
2 Drying towers, filled with ascarite and anhydrone.

Preparation of the apparatus

Dissolve 30 g silicon grease in ether (see remark 2), add 100 g sterchamol and evaporate the ether whilst stirring. Transfer the dry material into a suction flask, connect the suction opening with the inlet of the spiral tube, plug the opposite end of the tube with cotton wadding, slant the flask and draw the material into the tube by suction.

Heat the column to 200°C. Connect the furnace to the mains and keep the temperature at 800°C.

Lead nitrogen through the column at the rate of 2 l/h and supply oxygen before the furnace at the rate of 1.5 l/h by means of the injector.

After the amount of CO_2 issuing from the column has become constant, change the flow rates to 1.0 l/h (nitrogen) and 0.5 l/h (oxygen) and run a blank (consumption of sodium methylate per minute = v_0 ml).

Procedure

Stop the oxygen supply and raise the flow rate of the nitrogen current to 2.0 l/h.

Put 10 ml pyridine and about 2 mg thymol blue in the titration vessel after connecting it to the furnace.

Weigh an appropriate amount of sample (= a mg) into a platinum or nickel boat. Close the cock of the titration vessel, remove the rubber stopper from the column, push the boat rapidly into the heated zone of the column and start the stop watch while closing the column with the rubber stopper. Open the cock of the titration vessel immediately and pass oxygen through the furnace at the rate of 1 l/h (see remark 3). After t_1-4 minutes (t_1 being the experimentally determined period after which the naphthalene fraction starts issuing from the column) decrease the flow rate of the nitrogen to 1.0 l/h and the flow rate of the oxygen current to 0.5 l/h (see remark 5). Keep the pyridine just neutral and read the level of the 10 ml burette every minute until, after t_2 minutes, the amount of methylate consumed has become equal to that of the blank (total consumption of methylate = v_1 ml). Finally expel other compounds from the column (see remark 4).

Calculation

$$\frac{\left\{v_1-(t_2-t_1)v_0\right\} t\ 12.8}{a}\ 100 = \text{weight \% naphthalene}$$

Remarks

1. The first component issuing after the naphthalene consists mainly of methylnaphthalene, a large portion of the second fraction being dimethylnaphthalene.
2. Removal of the volatile components in the silicon grease by pretreatment with ethyl acetate and ethanol reduces the blank value.
3. The retention time of a component on the column is determined i.a. by the flow rate of the nitrogen led through the column. For this reason the flow rate has to be kept within reasonable limits.
   The flow rate of the oxygen must be lower than that of the nitrogen.
4. To remove higher-boiling components from the column, nitrogen is led through in the opposite direction at the rate of 5 l/h.
5. Reduction of the gas flow rate is only necessary if the separation effected at the normal rate is insufficient.

ACKNOWLEDGEMENT

The authors are much obliged to Dr. H. W. DEINUM for his continued interest and encouragement and to T. SMEETS for his assistance in the experimental work.

SUMMARY

Methods are described for the determination of small amounts of benzene (∿ 100 p.p.m.) and varying percentages of naphthalene (0.5-30%) in wash oil. The methods also enable other components of the wash oil to be determined. They are based on the separation of the components on a vapour phase chromatographic column and subsequent analysis. For this purpose an inexpensive detection method is used which is based on combustion of the separated components and immediate titration of the carbon dioxide formed.

RÉSUMÉ

On décrit des méthodes de détermination de petites quantités de benzène (∿ 100 mg/kg) et de pourcentages variés de naphtalène (0.5-30%) dans l'huile de lavage. Par ces méthodes, on peut déterminer également d'autres composants de l'huile de lavage. Ces méthodes sont basées sur la séparation des substances dans une colonne à chromatographie gaz-liquide. Pour la détection des substances on utilise une méthode exigeant un appareillage simple; les substances sont brûlées et l'anhydride carbonique formé est titré immédiatement.

ZUSAMMENFASSUNG

Beschrieben werden Methoden zu der gaschromatographischen Bestimmung kleiner Benzolmengen (∿ 100 mg/kg) und verschiedener Gehalte an Naphtalin (0.5 bis 30%) in Waschöl. Die Methoden ermöglichen weiterhin die Bestimmung anderer Bestandteile des Öls. Zur Identifizierung der chromatographisch getrennten Fraktionen wird eine wenig Apparatur erfordernde Methode verwendet. Die Fraktionen werden verbrannt und das gebildete Kohlendioxyd wird sofort titriert.

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2,6-BIS (4-PHENYL-2-PYRIDYL)-4-PHENYL-, AND 2,6-BIS (6-PHENYL-2-PYRIDYL)-4-PHENYLPYRIDINE. THEIR SPECTROPHOTOMETRIC CONSTANTS IN REACTIONS OF CHELATION WITH Fe(II), Cu(I) AND Co(II).

by

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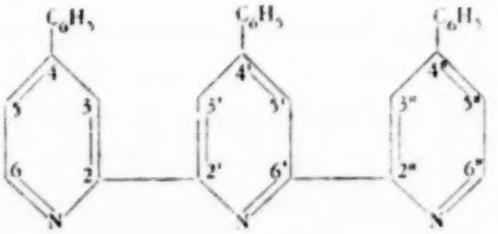
INTRODUCTION

Substitutions for the 4,4′,4″ positioned hydrogen of terpyridine by CH_3 and or C_6H_5 has previously been demonstrated to favorably modify their properties in chelation with Fe(II) and Co(II). Similar effects have been found in the case of dipyridines, diquinolines, and 1,10-phenanthrolines, (substitutions in the 4,4′ positions of the dipyridines and diquinolines and the 4,7-positions of 1,10-phenanthroline). The sensitivity is markedly altered in magnitude and solubility of the complexes in organic solvents is augmented, without loss in specificity.

Organic chelation reagents having the functional group, $=\overset{|}{N}\text{-}\overset{|}{C}\text{-}\overset{|}{C}\text{-}\overset{|}{N}=$, have been synthesized to the number of approximately 175 individual compounds. From the present and previous investigations, it has been shown that substitutions by methyl, ethyl, and phenyl groups, in positions para to the nitrogens of the active functional group, modify to the greatest extent the spectrophotometric constants which are basic in their applications in trace element determinations. Substitutions for the the 2,9-positions in 1,10-phenanthrolines on the part of methyl or phenyl groups constitute the next most important alterations in property. In such cases chelation with Fe(II) is prevented with retention of chelation for Cu(I). The same is true for substitutions in the 6,6′ positions of the dipyridines. (The diquinolines constitute a special case with duplicate effect.)

The structural formula for 2,6-bis(4-phenyl-2-pyridyl)-4-phenyl pyridine is as follows:



The synthesis of this compound was first proposed by SMITH AND WILKINS[1] and the trivial name "terosite" applied. This compound having hydrogens in place of the phenyl groups is terpyridine. With the 4′- positioned hydrogen of terpyridine only substituted by the phenyl group the product has the trivial name[1] "terosole".

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The compound having the 4,4″ positions of terosole replaced by methyl groups has the trivial name "terosine".

Terosite, the subject of the present work, has the highest molecular extinction coefficient in its Fe(II) chelation of any reagent owing its reactivity to the presence of the same functional group, $=N\text{-}\overset{\|}{C}\text{-}\overset{\|}{C}\text{-}N=$.

EXPERIMENTAL

Preparation of terosite

This synthesis was carried out by Professor F. H. CASE and T. KASPER, Temple University, and will be described, together with related compounds in a subsequent publication. Measures are being activated leading to its commercial availability.

Reagent solubility

Terosite is insoluble in water and ethanol even at comparitively low pH values. It is also insoluble in dioxan and ethyl acetate with or without added ethanol. It is soluble in chloroform or in equal parts by volume chloroform and ethanol. These solubility relationships restrict its use to extraction procedures in the spectrophotometric determination of iron. The purple complex with Fe(II) may be thus formed in solutions of pH 1.9 and higher and the complex extracted by chloroform-ethanol solvent. Color stability is provided in the range 2-8 in pH.

Determination of spectrophotometric constants

Buffer solution, (pH 5—5 ml) and 2 ml of hydroxylamine hydrochloride (iron free) are transferred to a 60 ml separatory funnel. A weighed sample of standard iron solution is added from a weight buret followed by 4 ml of 0.0025*M* reagent in chloroform-ethanol solution, (1:1 v/v). Add 3 ml of chloroform and 5 ml of ethyl alcohol. After shaking 30-60 seconds transfer the extracted complex and excess reagent to a 10 or 25 ml volumetric flask and dilute to the mark with ethanol. The absorbancy is then determined compared to a blank without added iron using a recording Model 11 Carey spectrophotometer. The results are given in Table I.

TABLE I

DETERMINATION OF THE MOLECULAR EXTINCTION COEFFICIENT OF TEROSITE AT WAVELENGTH 383 AND 583 mμ, Fe(II) CHELATION

Wt. Fe soln. g	*Wt. Fe* mg	*Vol of extract* ml	*Absorbancy* 383 mμ	583 mμ	*Molar extn. coeff.* ε 383 mμ	583 mμ
0.1216	0.01414	10	0.530	0.760	20,930	30,020
0.3070	0.0357	10	1.295	1.857	20,260	29,050
0.4543	0.0528	25	0.795	1.190	21,040	31,500
					Av. 20,740	Av. 30,200

The spectrophotometric absorption spectra of the terosite-iron complex

The absorption spectra of the terosite-ferrous iron complex leading to the values in Table I are reproduced in Fig. 1. The wavelengths of maximum absorption were thus found to be at 383 mμ and 583 mμ as shown. These maxima are characterized by notably sharp peaks at both wavelengths which are characteristically widely separated (200 mμ). Marked absorption is indicated in the near ultra-violet region.

The ferrous complex is very stable against oxidation by air and remains unchanged upon storage in stoppered containers. Permanent standards, if employed, may in time deposit fine crystals of excess reagent. This may be prevented by increasing the proportion of chloroform employed. The molar extinction coefficient of the ferrous complex terpyridine, terosine, terosole, and terosite[1], are thus respectively: 12500, 22000, 26300, and 30200. This is an outstanding demonstration of the influence of substitution in terpyridine at positions para to the nitrogen atoms. Through the influence of a high molar extinction coefficient, coupled with increased sensitivity by extraction of the colored complex into a limited volume, and by the use of 5 cm absorption cuvettes it is possible, employing terosite, to determine traces of iron in the range of parts per billion.

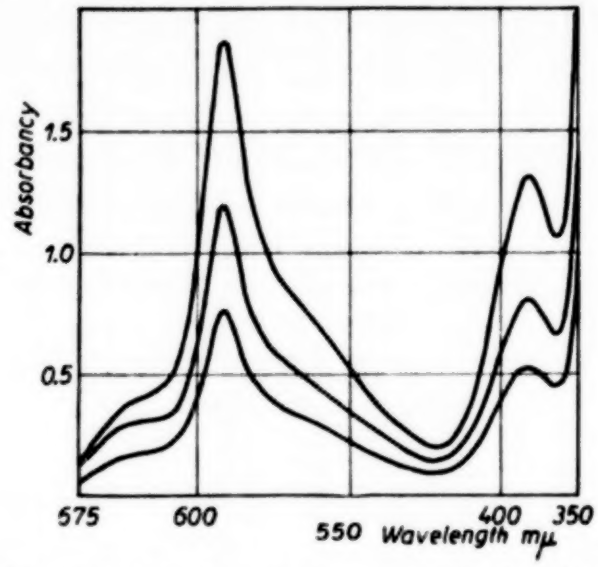

Fig. 1. Terosite-Fe(II) complex. Spectrophotometric absorbancy-absorption graph.

The spectrophotometric absorption spectra of the terosite-cobalt complex

The procedure employed in the preceding section applies to the formation of the complex with cobalt employing terosite with the substitution of cobalt for iron as the only modification. The absorption spectrum of the cobalt complex is shown in Figure 2. The range of color stability is pH 4 to pH 8.

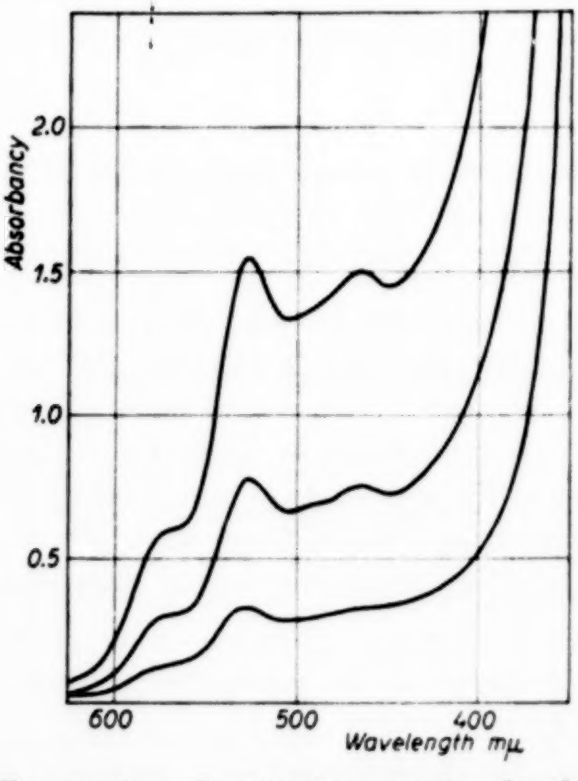

Fig. 2. Terosite-Co(II) complex. Spectrophotometric absorbancy-absorption graph.

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The absorption maxima as shown in Fig. 2 are at 466 and 528 mμ with an indication again of high absorption in the near ultraviolet. The absorption peaks are fairly sharp and are distinguished by virtue of almost equal intensity. The stability of the extracted solution of the complex with excess reagent is very good. The tendency for the excess reagent to crystallize out upon storage of the extraction medium may be prevented by the use of chloroform in place of ethanol in diluting the extracted fraction to volume in the volumetric flask prior to its evaluation spectrophotometrically.

The data involving cobalt from which the graph of Fig. 2 resulted are given in Table II.

TABLE II

THE MOLECULAR ABSORPTION COEFFICIENTS OF THE TEROSITE-COBALT COMPLEX (VOLUME OF EXTRACT = 10 ml)

Wt. Co soln. g	*Wt. Co* mg	*Absorbancy*		*Molar extinction coefficient,* ε	
		466 mμ	*528 mμ*	*466 mμ*	*528 mμ*
0.5493	0.0648	0.330	0.330	3004	3004
1.2266	0.1445	0.755	0.788	3078	3184
2.4367	0.2872	1.498	1.545	3074	3170
				Av. 3052	Av. 3120

The sensitivity of terosite in cobalt chelation, although only 10% of that for the same reagent in Fe(II) chelation, is augmented through its extractibility. Coupled with a high specificity the development of quantitative applications should prove attractive. Preliminary separation of metal interferences in the application of other spectrophotochemical procedures in the estimation of cobalt would thus be unrequired. A further advantage would exist in the simultaneous determination of cobalt and iron as suggested in the following section.

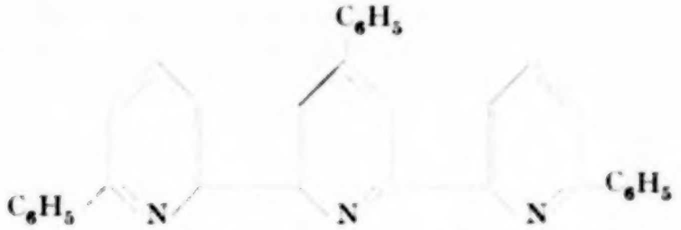
The ε values for the cobalt complexes of terpyridine, terosine, terosole and terosite are respectively: 1240, 2690, 2514, and 3120 for wavelengths, 506, 517, 519, and 528 mμ.

The simultaneous determination of cobalt and iron employing terosite as chelation reagent

It will be seen by examination of the spectrophotometric curves in Figures 1 and 2 that at 450 mμ the absorption for the terosite-ferrous iron complex is at its lowest value. By comparison the absorption for the terosite-cobalt complex is practically at its maximum value. At a wavelength of 583 mμ the absorptions of both the iron and cobalt complexes are of favorable magnitude for the second observation. By application of the formulation and solution of two appropriate simultaneous equations incorporating values from these observations as described by Mellon[2], values for both cobalt and iron may be obtained.

The copper(I) chelation complex of an additional phenyl substituted terpyridine (2,6-bis(6-phenyl-2-pyridyl)-4-phenylpyridine)

The structural formulation of this substituted terpyridine is:



This organic reagent, unlike any of the three phenyl substituted terpyridines previously discussed, (as well as terpyridine itself), gives a highly colored Cu(I) complex. This reagent was synthesized by those previously cited, (F.H.C. and T.K.), and the procedure is to be described elsewhere. The absorption spectrum of this new organic chelate as the Cu(I) complex is shown in Fig. 3.

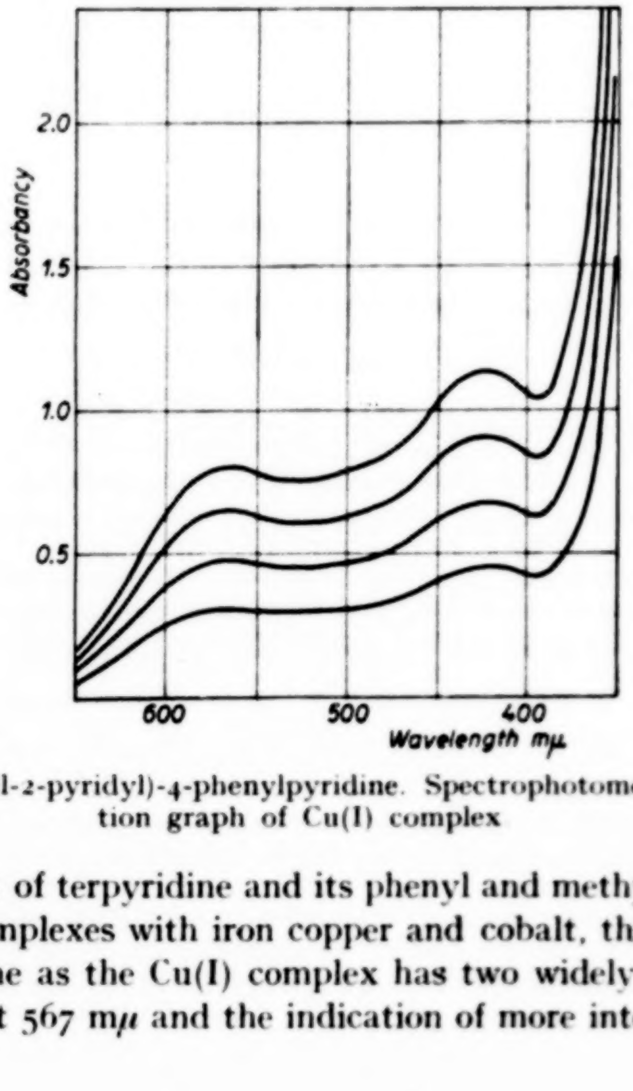


Fig. 3. 2,6-Bis(6-phenyl-2-pyridyl)-4-phenylpyridine. Spectrophotometric absorbancy-absorption graph of Cu(I) complex

As is characteristic of terpyridine and its phenyl and methyl substitution derivatives as the metal complexes with iron copper and cobalt, this particular triphenyl substituted terpyridine as the Cu(I) complex has two widely separated absorption maxima at 423 and at 567 mμ and the indication of more intense absorption in the near U.V.

The molecular absorption coefficients of 2,6-bis(6-phenyl-2-pyridyl)-4-phenylpyridine as the copper(I) complex

This triphenyl terpyridine derivative does not form either a Fe(II) or Co(II) complex. It is insoluble in water and ethanol, soluble in chloroform or its mixture with ethanol and soluble in isoamyl alcohol. The Cu(I) complex is stable in the pH range 2-8.2 and is rapidly formed at pH 5 from aqueous ethanol solutions. The reagent is conveniently employed as a 0.005*M* solution in mixed choroform-ethanol (1:1, v/v).

In determination of the molecular absorption coefficients for the Cu(I) complex, 5 ml of buffer solution, (pH 5), and 2 ml of 10% hydroxylamine hydrochloride solution are placed in a 60 ml separatory funnel. Weighed portions of standard copper solution are added followed by 2 ml of 0.005*M* complexing agent. Add 4 ml of chloroform and 5 ml of ethanol. Shake well, allow the extracted materials to separate out of the reaction mixture. Draw off the organic layer into 10 ml graduated flasks and dilute to volume with ethanol. The results from a series of determinations shown graphically in Fig. 3 are given in Table III.

TABLE III

THE MOLECULAR EXTINCTION COEFFICIENTS OF THE COPPER(I) COMPLEX OF 2,6-BIS(6-PHENYL-2-PYRIDYL)-4-PHENYLPYRIDINE (VOLUME OF EXTRACT = 10 ml)

Wt. Cu solution 2.01×10^{-6} moles/g *g*	*Absorbancy*		*Molar extinction coefficient, ε*	
	423 mμ	*567 mμ*	*423 mμ*	*567 mμ*
0.4832	0.448	0.305	4613	3140
0.7336	0.675	0.475	4578	3221
1.0074	0.905	0.650	4469	3210
1.2699	1.130	0.805	4427	3154
			Av. 4522	Av. 3181

ACKNOWLEDGEMENT

This work has been made possible only through the valued cooperation of Professor FRANCIS H. CASE and associates at Temple University, Philadelphia, U.S.A.

SUMMARY

The determination of the spectrophotometric constants of metal chelates of the newly prepared triphenyl derivatives of terpyridine, (λ_{max} and ε), have been made for 2,6-bis(4-phenyl-2-pyridyl)-4-phenylpyridine and 2,6-bis(6-phenyl-2-pyridyl)-4-phenylpyridine. The former forms stable complexes with Fe(II) and Co(II) both of which have unusual value in the trace element determination of these transition metals (the Fe(II) complex with an ε value of 30200 at 583 mμ is the most sensitive chelation reagent of its type at present known). The latter reagent forms a Cu(I) complex (to differentiate it from the former reagent) of rather low ε values only. A proposed procedure for the simultaneous determination of both iron and cobalt has been outlined.

RÉSUMÉ

Une détermination des constantes spectrophotométriques (λ_{max} et ε) a été effectuée sur les chélates métalliques de 2 dérivés triphénylés de la terpyridine récemment préparés: la 2,6-bis (4-phényl-2-pyridyl)-4-phénylpyridine; et la 2,6-bis(6-phényl-2-pyridyl)-4-phénylpyridine). Le premier donne des complexes stables avec Fe(II)et Co(II); il est très avantageux pour doser des traces de ces éléments de transition (le complexe de Fe(II) présentant une valeur de ε de 30200 à 583 mμ, est le plus sensible réactif de chélation de ce type, connu jusqu'à présent). L'autre réactif forme un complexe de Cu(I) (ce qui le différencie du premier réactif) de relativement faible valeur de ε. Une méthode a été établie pour le dosage simultané du fer et du cobalt.

ZUSAMMENFASSUNG

Die spektrophotometrischen Konstanten λ_{max} und ε wurden für Metallchelate von 2 neu hergestellten Triphenylderivaten des Terpyridins, 2.6-Bis(4-phenyl-2-pyridyl)-4-phenylpyridin und 2.6-Bis(6-phenyl-2-pyridyl)-4-phenylpyridin bestimmt. Ersteres bildet mit Fe(II) und Co(II) stabile Komplexe, welche für die Bestimmung von Spuren dieser Metalle ausserordentlich wertvoll sind (der Eisen(II)-Komplex ist mit einem ε-Werte von 30200 bei 583 mμ das empfindlichste bisher bekannte Reagenz dieser Art). Das andere Reagenz bildet (zum Unterschied vom erstgenannten) einen Cu(I)-Komplex mit eher niedrigen ε-Werten. Ein Verfahren zur gleichzeitigen Bestimmung von Eisen und Kobalt wird beschrieben.

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THE DETERMINATION OF MOLYBDENUM IN ITS BINARY ALLOYS WITH URANIUM BY HIGH-PRECISION SPECTROPHOTOMETRY

by

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INTRODUCTION

In a general study of the peroxy complexes of the elements of the transition series of groups IV, V and VI, PALILLA and co-workers[1] found that the molybdenum complex was stable over acidities ranging from 18M down to 1.5M in sulphuric acid. Weaker acidities were not studied. From this work two acidity ranges appeared possible for the absorptiometric determination of molybdenum as its peroxy complex. With solutions from 14 to 18M in sulphuric acid, the molybdenum peak is fairly stationary with maximum absorbancy in the region from 400 to 410 mμ. Although such strongly acidic solutions can be used in absorptiometric work they are not recommended if alternative conditions are available. In the case of this element, there is a second range which is applicable to solutions less than 9M in sulphuric acid. The molybdenum peak is again stationary, but it now occurs in the region of 325 mμ. These solutions are more convenient to handle and, in addition, the absorbancy index for the molybdenum complex is at least twice the value in the strongly acid solutions. These conditions should be applicable to the determination of the molybdenum content of uranium binary alloys, if the contribution from the uranyl ions at the wavelength used for absorbancy measurements is small and reproducible. The application of differential high precision spectrophotometry to this determination is reported in this paper.

EXPERIMENTAL

The behaviour of uranium

Before investigating the determination of molybdenum some knowledge of the behaviour of uranium was needed so as to be able to assess the probable interference of this element in the analysis of uranium-molybdenum mixtures. Preliminary experiments were, therefore, carried out to study the behaviour of uranyl ions under the solution conditions employed for the formation of the molybdenum peroxide complex. Results showed that hydrogen peroxide does not affect the absorption of uranyl sulphate solutions, at least over the acidity range from 2 to 5M. Graphical plots of the absorption spectra over the region from 350 to 400 mμ for uranyl sulphate solutions 0.5, 3 and 18M in sulphuric acid are shown in Fig. 1. It can be seen that the minimum absorption occurs in the limited region from 360 to 380 mμ and the absorbancy is fairly constant for solutions 0.5 to 3.0M in sulphuric acid. Because of this limited region for taking absorbancy measurements, changes in slit width will affect the absorbancy values and any increase in beam width, which allows light of less than 360 mμ or greater than 380 mμ to pass through the solution, will result in a large increase in the absorption caused by uranium. From these results, therefore, it may be possible to determine molybdenum in the presence of uranium when absorbancy measurements are taken in the region from 360-380 mμ and the slit width is carefully controlled to meet the above requirements. As can be seen from Fig. 2, although this wavelength region is away from the wavelengths for the peak, there is still an appreciable absorption by the molybdenum-peroxide complex.

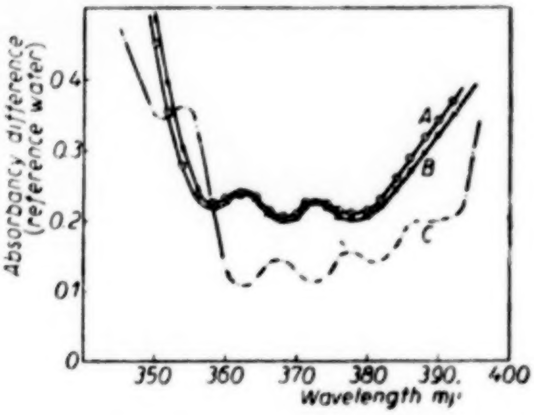


Fig. 1. Absorption spectra for uranyl sulphate solutions in the region 350 to 400 mμ.
Uranium 15 g/litre, Beckman 1 cm cell, slit width 0.10 mm.
● A H_2SO_4 0.5M, × B H_2SO_4 3.0M,
● C H_2SO_4 18.0M.

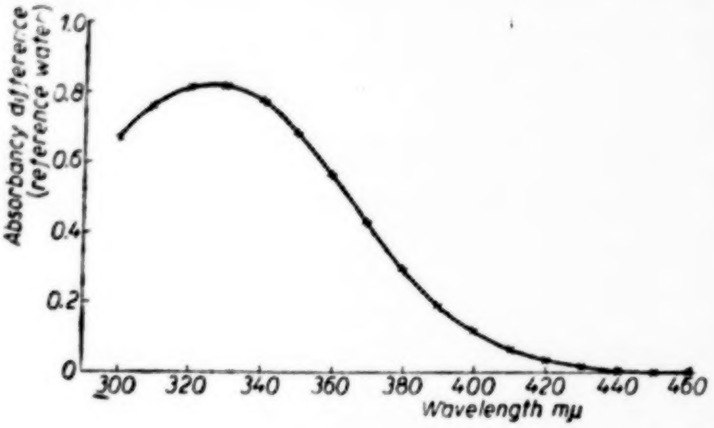
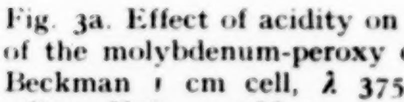


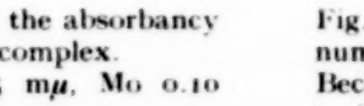
Fig. 2. Absorption spectrum for molybdenum-peroxy complex.
Molybdenum 0.08 g/litre, H_2SO_4 1.44M, H_2O_2 0.018M, Beckman 1 cm cell.

A study of the molybdenum-hydrogen peroxide complex

(1) *The effects of acidity, peroxide concentration, temperature and time*

Since the final sulphuric acid concentration needs to be less than approximately 3M, the behaviour of the absorbancy of the molybdenum peroxy complex was studied in this range using a constant hydrogen peroxide concentration of 0.09M. The molybdenum concentration was fixed at 0.1 g per litre and absorbancy measurements referred to water were obtained at a wavelength of 375 mμ. From the graphical plot of absorbancy readings against acidity in the range 0.2 to 3M in sulphuric acid (Fig. 3a), variations in acidity have least effect on the absorbancy at a 1.5M concentration of sulphuric acid.





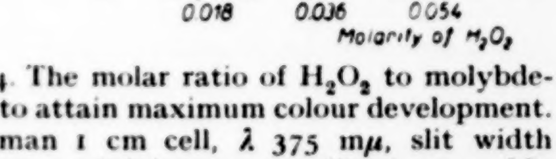


Fig. 3a. Effect of acidity on the absorbancy of the molybdenum-peroxy complex.
Beckman 1 cm cell, λ 375 mμ, Mo 0.10 g/litre, H_2O_2 0.09M.
Fig. 3b. Effect of hydrogen peroxide concentration on the absorbancy of the molybdenum complex.
Beckman 1 cm cell, λ 375 mμ, Mo 0.10 g/litre, H_2SO_4 1.5M.

Fig. 4. The molar ratio of H_2O_2 to molybdenum to attain maximum colour development.
Beckman 1 cm cell, λ 375 mμ, slit width 0.28 mm, molybdenum 0.12 g/litre (0.00125M), H_2SO_4 1.44M.

The effect of the hydrogen peroxide concentration was studied in experiments with the sulphuric acid concentration constant at 1.5M and with a molybdenum concentration of 0.10 g per litre. From Fig. 3b it is clear that a large excess of hydrogen peroxide intensifies the molybdenum colour, but in the region of 0.05M hydrogen peroxide, the error introduced by lack of control of the peroxide concentration is very small. The concentration of hydrogen peroxide needed to produce the full colour development of 0.12 g per litre of molybdenum is shown in Fig. 4, and from this it can be deduced that a 0.05*M* concentration of hydrogen peroxide is sufficient for molybdenum concentrations up to about 0.3 g per litre.

A study of the stability of the molybdenum-peroxy complex showed that no variation in absorbancy occurred from 2 minutes to about 30 minutes after the addition of the hydrogen peroxide and dilution of the solution to volume with water. In cases where the hydrogen peroxide content was barely sufficient to ensure maximum colour development, a slight fade in the colour intensity occurred. An investigation of the temperature coefficient by differentially measuring the absorbancy of a molybdenum solution at a constant temperature against others with the same molybdenum concentration but at different temperatures in the range 18 to 30°C, showed that a deviation of 1°C resulted in a change in the absorbancy of 0.17% (see Fig. 5).

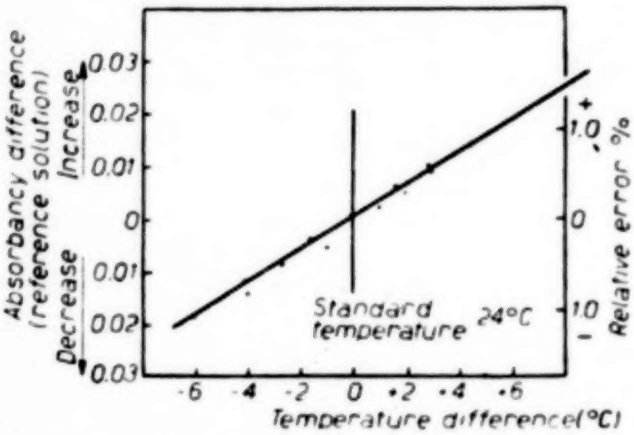


Fig. 5. Relative error for deviations from standard temperature.
Beckman 1 cm cell, λ 368 mμ, slit width 2.0 mm. Reference solution 0.34 g/l Mo (A = 1.67), H_2SO_4 1.44*M*, H_2O_2 0.18*M*.

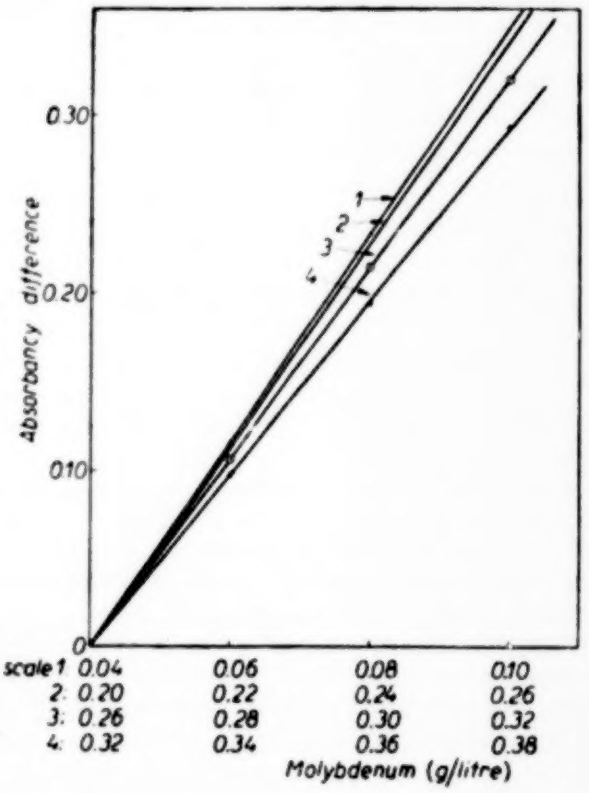


Fig. 6. Calibration graphs for molybdenum by high-precision spectrophotometry.
Beckman 1 cm cells, temperature 23°C, H_2SO_4 1.44*M*, H_2O_2 0.18*M*.
Slit widths:
1. <0.5 mm (4 mμ) 3. 1.5 mm (12 mμ)
2. 1.0 mm (8 mμ) 4. 2.0 mm (16 mμ)

(2) *Precision measurements of the molybdenum complex at 368 mμ*

Ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, is obtainable in a high state of purity. However, before using material for the preparation of standard solutions of molybdenum, verification of the composition is desirable and can be obtained by igniting suitable amounts to constant weight in the temperature range from 600 to 700°C[3]. Although a white powdery film tends to form on the surfaces of ammonium molybdate crystals, the change in composition is extremely small. This is illustrated by the molybdenum oxide yields, given in the following results, for a single crystal of the material brushed free of white powder and a sample of "fines" from the same bottle containing a high proportion of the powdered material.

Ignition times and temperature	$\frac{\textit{Experimental yield of } MoO_3}{\textit{Theoretical yield of } MoO_3} \times 100$	
	Single crystal	Powdered material
60 minutes at 600°C	100.02(9)	100.00(9)
Re-ignited 30 minutes at 700°C	100.00(2)	99.98(2)
Re-ignited 30 minutes at 700°C	99.99(5)	99.97(5)

Suitable solutions for precision measurements were, therefore, prepared by weighing the amounts of ammonium molybdate given in Table I into 250 ml conical beakers, followed by solution in about 20 ml of warm water. After the addition of 20 ml of 50% v/v sulphuric acid and suitable cooling, each solution was diluted to exactly 50 ml at a temperature of 23°C. Using the same pipette, a 5 ml aliquot of each solution was transferred to separate 50 ml graduated flasks. Then 6 ml of 50% v/v sulphuric acid was added to each flask followed by sufficient water to give a volume of 40 ml. After thermostating the flasks and contents at 23°C, 1 ml of hydrogen peroxide (100 volumes) was added to each and the volumes were adjusted to exactly 50 ml. The absorbancies obtained on these solutions by the solution reversing system are tabulated in Table I. These results, together with those for a narrower slit width, are also shown graphically in Fig. 6. Even at the maximum slit width used (2.0 mm), the Beer-Lambert law was found to be obeyed up to absorbancies of 1.8. From the graphs it will be seen, however, that the absorbancy index decreases as the slit width is increased. The magnitude of the errors in Table I confirms that high precision can be attained with this colour system.

TABLE I

ABSORBANCY MEASUREMENTS ON THE MOLYBDENUM-HYDROGEN PEROXIDE COMPLEX

Beckman, 368 mμ, 1 cm cells, temp. 23°C, 5 ml aliquot/50 ml, 1.44M H_2SO_4, 0.18M H_2O_2.

Am.mol/50 g	*Mo g/litre (coloured)*	*Slit width mm*	*Cell(1)*	*Cell(2)*	*Difference*	$\frac{\textit{Sum}}{2}$	*Absorbancy difference per 0.02 g/l molybdenum*	*Mean*	*Conc. error %*
0.1839(4)	0.20	1.0	+0.006	−0.007	0.013	−0.0005	0		
0.2023(3)	0.22	1.0	0.123	0.107	0.016	0.115	0.1150		+0.06
0.2207(2)	0.24	1.0	0.235	0.221	0.014	0.228	0.1140	0.1142	−0.02
0.2391(2)	0.26	1.0	0.348	0.334	0.014	0.341	0.1136		−0.04
Standard deviation ±0.0007 A									
0.2391(2)	0.26	1.5	+0.008	−0.008	0.016	0	0		
0.2575(1)	0.28	1.5	0.114	0.098	0.016	0.106	0.1060		+0.04
0.2759(0)	0.30	1.5	0.217	0.203	0.014	0.210	0.1050	0.1054	−0.03
0.2943(0)	0.32	1.5	0.324	0.308	0.016	0.316	0.1053		−0.01
Standard deviation ±0.0006 A									
0.2943(0)	0.32	2.0	+0.010	−0.009	0.019	−0.0005	0		
0.3126(9)	0.34	2.0	0.107	0.087	0.020	0.097	0.0970		−0.005
0.3310(8)	0.36	2.0	0.205	0.183	0.022	0.194	0.0970	0.0971	−0.005
0.3494(8)	0.38	2.0	0.302	0.282	0.020	0.292	0.0973		+0.010
Standard deviation ±0.0002 A									

The determination of molybdenum in the presence of uranium

Although slit widths up to 2 mm were used for the absorptiometric measurements with molybdenum alone, the maximum slit width that can be used in the presence of uranium is limited by the absorption interference of this element. Experiments on the determination of molybdenum in the presence of various amounts of uranium at different slit widths of the Beckman spectrophotometer showed that with slit widths greater than 1.5 mm an increased interference resulted from the uranium and the absorbancy readings were not linearly proportional to the uranium content. These results are shown graphically in Fig. 7. Because of this behaviour slit widths were maintained at 0.5 mm for the molybdenum determination. This value limited the maximum absorbancy which could be measured accurately by the differential system to about 0.40. Reference solutions with greater absorbancies could only be used if the light source of the spectrophotometer was replaced by another source richer in light of wavelength 370 mμ. This would lead to improved meter sensitivity and an increase in accuracy. It is not claimed, therefore, that the proposed conditions are the most suitable to obtain accurate results.

Before this procedure could be applied to alloy analysis re-calibration of the spectrophotometer for the determination of molybdenum was necessary under the new conditions. A value for the correction factor to be applied for the uranium in solution was also required. The differential spectrophotometric procedure described in an earlier report was to be used for the uranium determination[2] and further investigation of this determination was not necessary. The calibration experiments were carried out using the procedure described earlier and the weights of ammonium molybdate shown in Table II. This table also contains the results of these experiments, the mean calibration factor being 0.173 g per litre of molybdenum for an absorbancy of 1.0. The uranium correction factor was determined by preparing several solutions containing 0.1 g per litre of molybdenum and increasing amounts of uranium. The absorbancy difference was then measured between these solutions and one without uranium. A correction factor of 1% uranium equal to 0.0023% molybdenum was obtained.

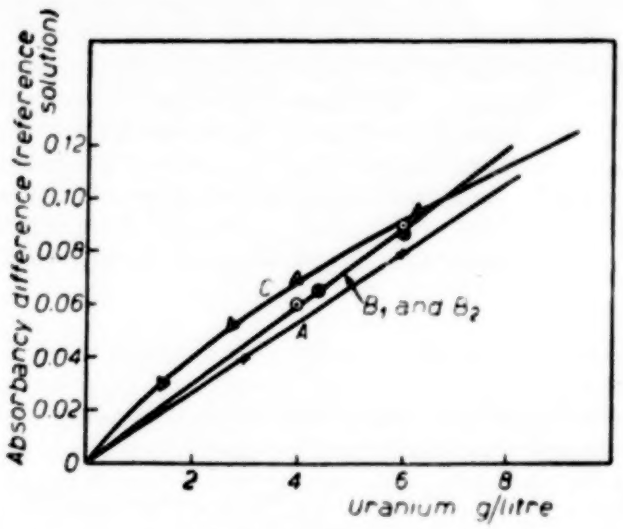


Fig. 7. Correction graphs for uranium.
Beckman 1 cm cell, λ 368 mμ.

	Molybdenum	Slit width	A's ratio U/Mo
A	nil	0.23 mm (1.4 mμ)	0.0023
B_1	0.20 g/l	1.0 mm (6.0 mμ)	0.0026
B_2	0.28 g/l	1.5 mm (9.0 mμ)	0.0027
C	0.30 g/l	2.0 mm (12.0 mμ)	—

A consideration of the absorbancy indices of uranium and molybdenum showed that for ratios of uranium to molybdenum exceeding 10, the correction for uranium in the molybdenum determination was greater than 2-5% of the molybdenum content. It is fortunate that high precision is not usually required for low alloying contents and even at 1% molybdenum, where the correction to be applied is equal to 25% of the molybdenum content, a 10% variation in the correction causes an error of only ± 0.025% molybdenum. At the other end of the alloying range where the molybdenum is greater than the uranium by a factor of 10, the correction to be applied (0.02%) is less than the maximum precision which can be attained. The system is particularly suitable, therefore, for uranium alloys with molybdenum contents greater than 90%, when an accuracy better than 99.9% could be attained by the differential method.

TABLE II

CALIBRATION

Beckman, 368 mμ, 1 cm cells, temp. 23°C, s.w. 0.50 mm, 5 ml aliquot/50 ml, 1.44M H_2SO_4, 0.18M H_2O_2.

Am.mol/50 g	*Mo g/l when coloured*	*Cell(1)*	*Cell(2)*	*Diff.*	*Sum/2*	*Absorbancy difference for 0.02 g/l Mo*	*Mean*	*Conc. error %*
0.0367(9)	0.04	+0.003	−0.003	0.006	0			
0.0552(8)	0.06	+0.117	+0.113	0.004	0.1150	0.1150		−0.17
0.0735(7)	0.08	+0.236	+0.230	0.006	0.233	0.1165	0.1155	+0.25
0.0919(7)	0.10	+0.348	+0.342	0.006	0.345	0.1150		−0.10
Standard deviation ±0.0009 A								
0.0919(7)	0.10	+0.003	−0.003	0.006	0	0		
0.1103(6)	0.12	+0.119	+0.113	0.006	0.116	0.1160		+0.13
0.1287(5)	0.14	+0.233	+0.227	0.006	0.230	0.1150	0.1152	−0.03
0.1471(4)	0.16	+0.348	+0.340	0.008	0.344	0.1147		−0.06
Standard deviation ±0.0007 A								

Mean calibration factor = 0.1730 g/l Mo/1.0 A

Procedure for the determination of molybdenum in uranium-molybdenum alloys

Dissolve 1 g of sample in 20 ml of 50% v/v sulphuric acid, using nitric acid to assist solution. Evaporate to fumes of sulphuric acid, cool, add 20 ml of water and re-fume to remove completely the nitric acid. Cool and dilute the solution to a volume of exactly 50 ml at a temperature of 23°C. Determine the uranium content of the sample by measuring differentially against appropriate uranium standards as described in a previous report[2].

For the molybdenum determination transfer 5 ml of the sample solution to a 50 ml volumetric flask and add 6 ml of 50% v/v sulphuric acid followed by water to make the volume approximately 40 ml. After thermostating at 23°C, add 1 ml of hydrogen peroxide (100 volume) and adjust the volume to exactly 50 ml. Measure the absorbancy of the solution differentially against appropriate molybdenum standards, using the solution reversing system. Take readings at a wavelength of 368 mμ using 1 cm cells and a slit width of 0.5 mm. In deriving the molybdenum content apply the correction factor for the uranium, 1% of uranium being equivalent to 0.0023% molybdenum.

Results

The procedure was first tested on synthetic alloy solutions prepared from uranium oxide U_3O_8 and ammonium molybdate and processed as described for alloys to give 50 ml of solution at 23°C. Aliquots were transferred to 50 ml volumetric flasks and solution conditions were adjusted to give 8 ml of 50% v/v sulphuric acid, 1 ml of hydrogen peroxide (100 volume) and approximately 5 mg of molybdenum per 50 ml. Absorbancy measurements were taken against a molybdenum standard of similar molybdenum concentration (0.1 g/litre) using the conditions described above. On applying the correction for uranium the satisfactory molybdenum recovery results shown in Table IIIA were obtained. It can be seen that when the molybdenum content is less than 5% and the correction for uranium is large (10% of the molybdenum content), the results obtained are in error by only about 1% of the molybdenum content. Table IIIB contains the results for two typical alloy samples of the type 90% uranium, 10% molybdenum. The close agreement of the results for duplicate determination on these samples confirms the suitability of this procedure in alloy analysis.

TABLE IIIA

RESULTS FOR THE ANALYSIS OF SYNTHETIC URANIUM-MOLYBDENUM ALLOYS

Composition of alloys(%) *Uranium*	*Molybdenum*	*Uranium Correction* *%Mo*	*Molybdenum(%)* *by analysis*	*Error* *%*
80	20.0	0.18	20.03	+0.15
80	20.0	0.18	19.95	−0.25
90	10.0	0.20	9.98	−0.20
90	10.0	0.20	10.00	nil
95	5.0	0.21	5.04	+0.80
95	5.0	0.21	5.01	+0.20
97.5	2.50	0.21	2.54	+1.60
97.5	2.50	0.21	2.48	−0.80

TABLE IIIB

RESULTS FOR THE ANALYSIS OF TYPICAL URANIUM-MOLYBDENUM ALLOYS

Sample No.	*Approximate composition(%)* *Mo*	*U*	*Mo (%)* *by analysis*	*Mean* *result*	*Deviation from* *mean % Mo*
1	10	90	9.88	9.90	−0.02
			9.92		+0.02
2	10	90	9.95	9.965	−0.015
			9.98		+0.015

References p. 579

SUMMARY

High-precision spectrophotometry has been applied to the determination of molybdenum by using the coloured complex formed by this element with hydrogen peroxide. This determination is best carried out from solutions about 1.5*M* in sulphuric acid and 0.18*M* in hydrogen peroxide. When absorbancy measurements are taken in the limited wavelength region of 360 to 380 mμ, the small interfering absorbancy from uranyl ions can be corrected for. A procedure has been developed for the determination of molybdenum in binary alloys containing uranium as the major constituent. This method is direct and rapid compared with gravimetric methods which require the preliminary separation of the molybdenum. For alloys containing more than 2.5% molybdenum a precision better than ± 1.0% can be attained. Below this level, uranium interference renders the method less precise.

RÉSUMÉ

Une méthode spectrophotométrique très précise a été appliquée au dosage du molybdène; elle est basée sur la formation d'un complexe coloré entre le molybdène et le peroxyde d'hydrogène. Il est avantageux d'effectuer ce dosage dans des solutions d'acide sulfurique, environ 1.5*M* et de peroxyde d'hydrogène, 0.18*M*. Lorsque les mesures se font entre 360 et 380 mμ, la faible absorption due aux ions uranyle peut être corrigée. Un procédé est proposé pour le dosage du molybdène dans des alliages binaires renfermant l'uranium comme constituant principal. Cette méthode est directe et rapide, comparée aux méthodes gravimétriques, ces dernières nécessitant une séparation préliminaire du molybdène. Pour les alliages renfermant plus de 2.5% de molybdène, une précision meilleure que ± 1.0% peut être obtenue. Pour des teneurs plus faibles, l'uranium diminue la précision.

ZUSAMMENFASSUNG

Eine sehr genaue spektrophotometrische Methode wurde zur Bestimmung von Molybdän angewendet; sie gründet sich auf die Bildung einer gefärbten Komplexverbindung zwischen Molybdän und Wasserstoffperoxyd. Es ist am besten, die Bestimmung in ca. 1.5*M* Schwefelsäure und 0.18*M* H_2O_2 auszuführen. Wenn die Absorption in dem kleinen Wellenlängenbereich 360 bis 380 mμ gemessen wird, kann man die durch die Absorption der Uranylionen verursachte geringe Störung korrigieren. Ein Verfahren zur Bestimmung von Molybdän in binären Legierungen welche Uran als Hauptbestandteil enthalten, wurde entwickelt. Im Vergleich zu den gravimetrischen Methoden, welche die vorherige Abtrennung des Molybdäns erfordern, ist diese Methode direkt und rasch zu nennen. Für Legierungen welche mehr als 2.5% Molybdän enthalten, konnte eine bessere Genauigkeit als ± 1% erzielt werden. Unterhalb dieser Grenze wird die Genauigkeit durch das Uran beeinträchtigt.

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DOSAGE DE RUTHÉNIUM EN SOLUTION DILUÉE PAR DILUTION ISOTOPIQUE ET SPECTROPHOTOMÉTRIE

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INTRODUCTION

Des recherches électrochimiques effectuées antérieurement sur le ruthénium[1] nous ont posé des problèmes analytiques dans un domaine de concentration très vaste allant de 10^{-2} à $10^{-10}N$ environ. Plusieurs méthodes analytiques ont été décrites dans la littérature. Nous allons en rappeler ici quelques exemples typiques.

La méthode principale est celle décrite par GILCHRIST ET WICKERS[2] et modifiée par d'autres auteurs. Elle consiste à oxyder le ruthénium en tétroxyde RuO_4, à distiller et absorber le tétroxyde dans une solution réductrice, à partir de laquelle on obtient par une nouvelle réduction le ruthénium métallique qui est pesé. Cette méthode est applicable à des quantités macroscopiques.

HOWE[3] a dosé le ruthénium en solution ($RuCl_4$) en le réduisant à l'état trivalent avec le chlorure d'étain(II) de titre connu. CROWELL ET YOST[4] ont établi deux méthodes pour le dosage du tétrachlorure de ruthénium; l'une par potentiométrie utilisant comme réducteur le sulfate de titane(III) (dans une atmosphère de CO_2); l'autre par réduction à l'état trivalent avec un excès d'iodure de potassium et dosage de l'iode libéré par une solution titrée de thiosulfate.

BRECKENRIDGE ET SINGER[5] ont établi une méthode colorimétrique de dosage de ruthénium sous forme de complexes chlorés, à l'aide de l'acide 5-hydroxyquinoléine-8-carboxylique. Cette méthode est satisfaisante pour des dilutions allant jusqu'à $5 \cdot 10^{-7}M$. Une autre méthode basée sur la couleur rouge brune du ruthénium(IV), en solution chlorhydrique, a été proposée par ZVYAGINTZEV[6]. D'autre part, DEFORD[7] a mis au point une méthode plus générale, utilisant la formation d'un complexe coloré avec la thiourée en solution chlorhydrique. Les différentes méthodes colorimétriques utilisées jusqu'en 1953 pour la détermination quantitative du ruthénium et des autres métaux du groupe du platine ont été discutées par BEAMISH ET BRYDE[8].

Ces diverses méthodes ne sont pas applicables d'une façon satisfaisante aux problèmes analytiques que nous avons eu à résoudre. La méthode gravimétrique implique des erreurs importantes par suite de la difficulté de réaliser une distillation et une absorption complète de RuO_4. Les méthodes volumétriques ne sont précises que pour des concentrations élevées ou moyennes. D'autre part, les procédés colorimétriques dans la mesure où ils sont applicables aux solutions très diluées ont été établis pour le milieu chlorhydrique. Nous avons essayé d'appliquer une de ces méthodes aux solutions sulfuriques (milieu de nos études électrochimiques) sans succès évident.

Par suite de ces considérations, nous avons été amené à élaborer de nouveaux procédés, dont deux font appel aux propriétés radioactives; un autre spectrophotométrique, s'applique au domaine de concentration compris entre $7.5 \cdot 10^{-4}$ et $10^{-5}N$ environ et enfin une méthode polarographique, pour des solutions aussi diluées que $5 \cdot 10^{-10}N$. Cette dernière fait l'objet d'un autre exposé[9] et ne sera donc pas décrite ici.

Ces recherches ont été effectuées en utilisant surtout des solutions sulfuriques de ruthénium(III). La préparation et la purification des solutions, ainsi que les techniques électrochimiques et radioactives, ont été déjà décrites[1].

Méthode des indicateurs radioactifs

Les deux méthodes radioactives que nous avons établies sont basées sur le principe de dilution isotopique. Dans l'une on utilise la distillation de RuO_4 marqué, dans l'autre le dépôt cathodique du ruthénium marqué.

A) Distillation de RuO_4

Une partie aliquote de la solution sulfurique de ruthénium(III) additionnée de Rd-Ru d'activité totale connue est oxydée anodiquement avec une densité de courant de 4 mA/cm² au moyen du dispositif représenté par la Fig. 1. Le tétroxyde de ruthénium formé, et entraîné par un courant gazeux, est absorbé dans une solution d'acide chlorhydrique concentrée à 0°C et ainsi réduit en ruthénium(IV). On mesure l'activité passée dans cette solution dans les mêmes conditions que pour la solution qui a servi pour l'électrolyse. On a ainsi le rapport entre l'activité de la solution chlorhydrique et celle de la soultion initiale avant l'oxydation et donc la distribution du ruthénium total entre les deux solutions. La valeur absolue du ruthénium de la solution chlorhydrique est déterminée gravimétriquement en précipitant l'hydroxyde, par l'hydroxyde de sodium à chaud, qu'on pèse à l'état de RuO_2 après avoir séché et calciné. Le résultat peut être vérifié en mesurant l'activité restante dans la solution électrolysée.

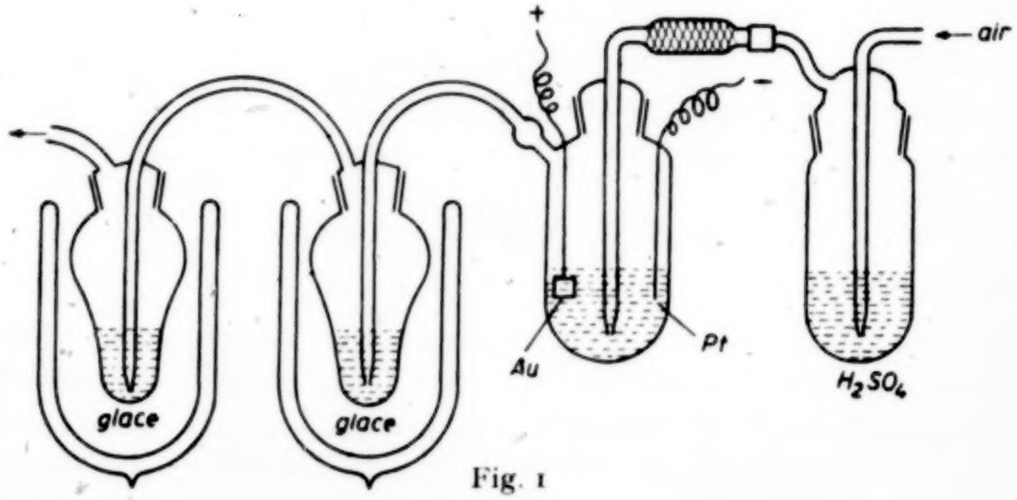

Fig. 1

Cette méthode que nous avons appliquée à des solutions de l'ordre de 10^{-2} à $10^{-3}N$

peut être utilisée pour la détermination quantitative de ruthénium en présence d'autres métaux et pour des concentrations plus élevées. On pourrait l'utiliser évidemment pour des solutions contenant initialement d'autres composés de ruthénium de diverses valences. Elle ne présente pas les difficultés rencontrées dans les procédés habituels qui nécessitent une distillation et une absorption complète de RuO_4. La précision de notre méthode peut être améliorée si l'on réduit avec du zinc la solution chlorhydrique de ruthénium(III) à l'état métallique qu'on pèserait sous cette forme. L'oxydation en RuO_4 peut être faite aussi par des moyens chimiques.

B) Dépôt cathodique

Cette méthode consiste à électrolyser à une température supérieure à 75°C, un volume connu de la solution mère, contenant une quantité déterminée de Rd-Ru, en séparant les compartiments anodique et cathodique par un siphon électrolytique. La réduction cathodique se poursuit pendant un certain temps qui dépend de la nature de la solution, de la densité du courant et de la température. Les meilleures conditions sont comprises entre 0.5 et 2 mA/cm^2 et entre 90 et 100°C.

On n'a pas intérêt à continuer l'électrolyse jusqu'à l'épuisement de l'activité. Après l'arrêt de l'électrolyse, on mesure l'activité en solution et on pèse le ruthénium déposé dont on mesure éventuellement l'activité. Ces données permettent de connaître la concentration initiale en ruthénium de la solution mère. Nous avons dosé par ce procédé des solutions de Ru^{III} et de Ru^{IV}.

Cette méthode est plus simple et plus rapide, mais ses applications sont moins étendues. On pourrait vraisemblablement l'utiliser pour quelques autres composés de ruthénium, mais il est impossible de l'appliquer directement à des valences supérieures à 4.

Nous avons appliqué ces deux méthodes au dosage d'une solution de ruthénium(III) exactement titrée par le thiosulphate. On a retrouvé la même valeur à ± 5% près.

Méthode spectrophotométrique

Principe de la méthode

La méthode qu'on a élaborée pour le microdosage du ruthénium en solution de concentration variant entre $7.5 \cdot 10^{-4}$ et 10^{-5} éq.g/l est basée sur la colorimétrie des solutions très diluées d'iode. Plusieurs procédés de microdosage spectrophotométrique d'iode sont décrits dans la littérature, dont celui de LAMBERT[10] qui est très précis mais laborieux. Nous avons surtout tiré profit des résultats obtenus au laboratoire Curie par Mme VERMEIL[11] pour le microdosage des phosphites par oxydation avec une quantité connue d'iode et détermination en retour de l'excès d'iode par spectrophotométrie en utilisant $\lambda = 410$ mμ et $\lambda = 325$ mμ.

Le principe de notre méthode consiste à oxyder la solution sulfurique de ruthénium(III) par un courant modéré de chlore, en ruthénium(IV) et à réduire ensuite celui-ci par l'iodure de potassium, l'iode libéré étant déterminé par spectrophotométrie à $\lambda = 410$ mμ. La quantité d'iode ainsi produite est équivalente au ruthénium dissous selon la réaction:

$$2\ Ru^{+4} + 2\ I^- \rightarrow 2\ Ru^{+3} + I_2$$

Pour avoir des résultats reproductibles, il faut que l'acidité de la solution à oxyder

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soit supérieure à la normalité, afin d'empêcher l'oxydation aux valences supérieures avec formation de tétroxyde de ruthénium volatil. Au contraire, au moment de la réduction, l'acidité doit être diminuée afin d'éviter la libération d'iode résultant de l'attaque de l'iodure de potassium par l'acide relativement concentré (le pH optimum est compris entre 2 et 4, d'après les résultats ci-dessus cités de Mme VERMEIL).

Courbe d'étalonnage et procédé expérimental

Toutes les mesures spectrophotométriques ont été effectuées à l'aide d'un spectrophotomètre Unicam (Cambridge). L'étude du spectre de la solution jaune de ruthénium(III) a montré qu'à $\lambda = 410$ mμ la densité optique due à ce composé est négligeable par rapport à celle d'une solution contenant une quantité équivalente d'iode. Par contre, à 325 mμ, le coefficient d'extinction de la solution de ruthénium(III) est trois fois plus grand qu'à 410 mμ. Les mesures ont donc été faites à 410 mμ.

Nous avons préparé des solutions d'acide sulfurique $0.4N$ en diluant 10 ml de la solution jaune de ruthénium(III) et une quantité appropriée d'acide de titre connu à 100 ml; on ajoute ensuite 2 g d'iodure de potassium. A l'aide de ces solutions et d'une solution d'iode $0.1N$ exactement titrée, on prépare une série de solutions de concentration comprise entre $7.5\cdot10^{-4}$ et 10^{-5} éq.g/l.

La mesure de la densité optique de ces solutions par rapport à la solution de $Ru^{III} + KI$, exempte d'iode, permet de tracer la courbe d'étalonnage, Fig. 2.

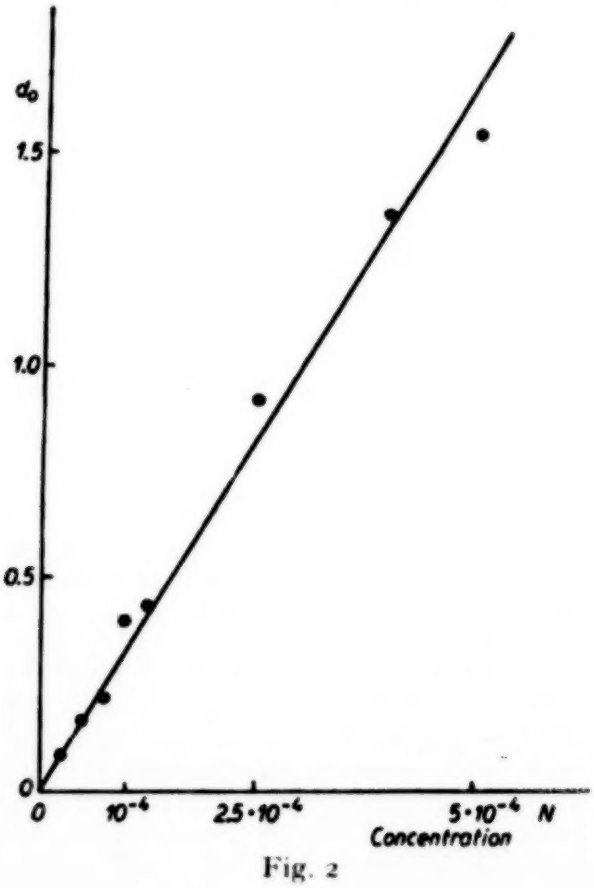

Fig. 2

Pour transformer le ruthénium trivalent de la solution à doser en ruthénium(IV) on acidifie 5 ml jusqu'à $4N$ et on fait passer un courant modéré de chlore pendant 10 minutes. On laisse ensuite la solution au repos pendant une heure et demie; puis on chasse l'excès de chlore en faisant bouillir doucement la solution pendant 10 minutes. Après refroidissement, la solution est transvasée dans une fiole jaugée de 50 ml, diluée à 45 ml environ et additionnée d'un gramme d'iodure de potassium; on complète à 50 ml. L'iode libéré est mesuré immédiatement au spectrophotomètre à $\lambda = 410$ mμ.

A l'aide de ce procédé, nous avons dosé une solution de ruthénium de concentration inconnue. On a opéré avec cinq parties aliquotes différentes de cette solution et on a trouvé une concentration de $2.5\cdot10^{-4}$ éq.g/l. Les résultats étaient reproductibles à ± 3%.

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Cette méthode pourrait s'appliquer à plusieurs autres composés de ruthénium. Les valences supérieures à 3 sont en général réduites quantitativement à la valence 3 par l'iodure de potassium, tandis que les valences inférieures pourraient être oxydées à l'état tétravalent par le procédé décrit ci-dessus.

REMERCIEMENTS

Je voudrais exprimer mes remerciements à Monsieur Haïssinsky pour l'aide et l'encouragement constants au cours de ce travail.

RÉSUMÉ

On a établi deux méthodes radioactives de dosage de ruthénium en solution (10^{-2}-$10^{-3}M$); l'une est basée sur l'oxydation partielle en tétroxyde de ruthénium marqué et l'autre sur le dépôt cathodique partiel de ruthénium métallique marqué.

On a, d'autre part, mis au point une méthode de dosage pour des solutions $7.5 \cdot 10^{-4}$ à $10^{-5}N$ en ruthénium par microdosage spectrophotométrique d'iode à $\lambda = 410$ mμ.

SUMMARY

Two radioactive methods have been established for the determination of ruthenium in solution (10^{-2}-$10^{-3}M$); one is based on the partial oxidation of labelled ruthenium to the tetroxide, and the other is based on the partial cathodic deposition of labelled metallic ruthenium.

Furthermore, a method of estimation has been perfected for solutions $7.5 \cdot 10^{-4}$ to $10^{-5}N$ with respect to ruthenium, by spectrophotometric microdetermination of iodine at $\lambda = 410$ mμ.

ZUSAMMENFASSUNG

Zwei Methoden zur Bestimmung von Ruthenium in Lösung (10^{-2}-$10^{-3}M$) werden beschrieben, welche sich auf Messung der Radioaktivität gründen; bei der einen wird das markierte Ruthenium teilweise zum Tetroxyd oxydiert und dieses destilliert, bei der anderen wird metallisches markiertes Ruthenium teilweise an der Kathode abgeschieden.

Zur Bestimmung von $7.5 \cdot 10^{-4}$ bis $10^{-5}N$ Lösungen wurde andererseits eine Methode entwickelt, die sich auf die spektrophotometrische Mikrobestimmung von Jod bei $\lambda = 410$ mμ gründet.

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POLAROGRAPHISCHE UNTERSUCHUNG VON TRINK- UND BRAUCHWASSER

DIE BESTIMMUNG DER HÄRTE UND DER ALKALIEN

von

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Zur Untersuchung von Trink- und Brauchwässern, also recht verdünnten Lösungen, bot sich die polarographische Methode seit jeher als besonders geeignet an. Bezüglich der Genauigkeit versprach sie natürlich weniger als die besten klassisch-analytischen Verfahren, an Selektivität, besonders aber an Schnelligkeit dagegen umso mehr.

Zur Beurteilung der natürlichen Wässer sind nun aber bekanntlich die Ca-, Mg- und die Alkaliionen die wichtigsten Kationen. Eine polarographische Wasseranalyse scheiterte bisher in erster Linie daran, dass das Mg^{+2}-Ion sich an der tropfenden Quecksilberelektrode nicht bestimmen liess, und dass auch die polarographische Bestimmung des Calciums recht unsicher ausfiel. Ausserdem konnte in Gegenwart von Erdalkalien auch die Bestimmung der Alkaliionen nicht einfach und besonders nicht gleichzeitig, d. h. mittels einer einzigen Aufnahme durchgeführt werden.

Nachdem es uns in jüngster Zeit gelungen ist das Problem der Polarographie des Magnesiums[1] mit Hilfe einer modifizierten strömenden Quecksilberelektrode[2] zu lösen, haben wir nun auf demselben Wege auch die Bestimmung des Calciums ausgearbeitet.

Die strömende Quecksilberelektrode wurde von J. Heyrovský eigentlich für die oszillographische Polarographie konstruiert. Ihre Vorteile auf diesem Gebiete sind der tropfenden Elektrode gegenüber wohl allgemein bekannt; um dieselbe aber auch in der klassischen (quantitativen) Polarographie verwerten zu können, mussten noch zwei weitere Bedingungen erfüllt werden:

1. Die Grösse der Elektrodenoberflächen, sowie der Abstand derselben darf sich während des Strömens nicht in geringstem Masse ändern.
2. Bei Neuauffüllung der Zelle sollen sich obige Abmessungen, um sämtliche Messungen quantitativ vergleichen zu können, automatisch einstellen.

Dies konnte nun bei der neuen Konstruktion (Fig. 1) auf folgende Weise erreicht werden: Das aus der Kapillare ausgespritzte Quecksilber fällt samt mitgerissener Lösung in das Elektrodengefäss zurück, wodurch die darin befindliche Elektrolytmenge konstant bleibt.

Das ausgeströmte Quecksilber sammelt sich im unteren Teile des Gefässes und sein Überschuss wird durch den Überlauf bei *a* vom Boden abgeleitet. Dieser besteht aus einer Röhre von 2-3 mm lichter Weite, deren Mündung zur Vermeidung einer Absaugwirkung knapp nach der Biegung vertikal abgeschnitten ist. So tritt das Quecksilber tropfenweise, jedoch trocken, d. h. ohne Mitnahme von Lösung aus. Die Schwankungen der Oberflächenhöhe des Quecksilbers im Gefässe, welches gleichzeitig als unpolarisierbare Elektrode (Kontakt bei *b*) dient, sind durchaus zu vernachlässigen, da die Tropfen gegen die Masse der Quecksilberfüllung bzw. gegen seine Oberfläche sehr klein sind.

Die Spritzkapillare *c*, welche übrigens nach Vorschrift von Heyrovský bereitet wurde, wird statt eines Gummischlauches mittels eines Schliffes angesetzt, wodurch dieselbe selbst nach

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Reinigung des Gefässes immer in die gleiche Lage kommt. Pipettiert man nun über das Quecksilber stets die gleichen Volumina der Elektrolyte, so hat man immer die gleichen Füllhöhen und hiermit bleibt auch die eintauchende Kathodenlänge (d. h. ihre Oberfläche) infolge obiger Vorkehrungen auch während des Strömens praktisch konstant. Sie könnte höchstens wegen der tropfenweise Ableitung des Anodenquecksilbers ganz geringen Schwankungen unterworfen sein, welche aber auch leicht aufgehoben werden können, indem man den Auffülltubus (*d*) verschlossen hält und ein Pufferröhrchen (*e*) anbringt, welches — falls notwendig — auch zur Einleitung eines indifferenten Gases dienen kann. So beobachtet man nur in dem Pufferröhrchen gewisse Schwankungen, die grosse Flüssigkeitsoberfläche bleibt aber völlig unbewegt.

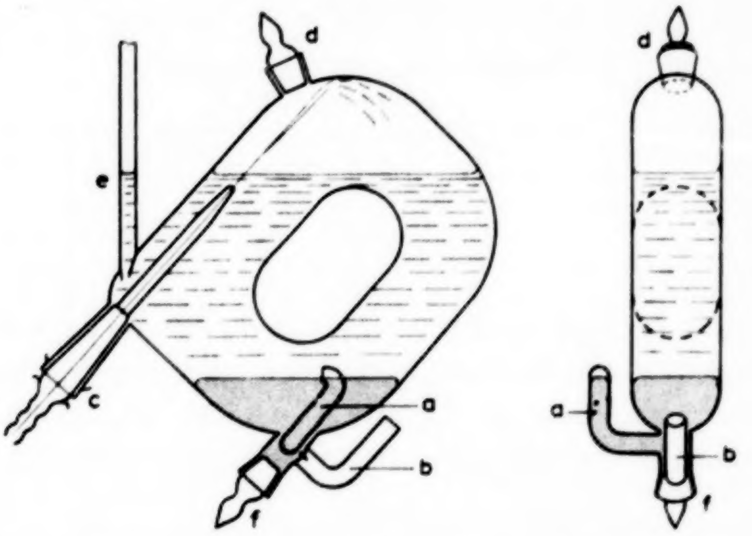

Fig. 1. Die modifizierte strömende Quecksilberelektrode

Das Gefäss wird in der gezeichneten Lage in einem Stativ befestigt und es kann über *f* vollständig entleert werden. Der Inhalt der Zelle beträgt etwa 20 ml.

Die Polarogramme wurden mit einem schreibenden Radiometer PO-3-Apparat aufgenommen, bei der Empfindlichkeit 5000 bzw. 10000 mit Kompensation 3 bzw. 2. Das zur Bereitung der Grundlösung verwendete $[N(CH_3)_4]Cl$ wurde aus dem käuflichen Jodid hergestellt, indem letzteres nach Umkrystallisieren mit einem 25%-igen Überschuss der berechneten Menge von *p.a.* AgCl verrieben, dann mit soviel reinstem destillierten Wasser geschüttelt wurde, dass die nach dem Filtrieren gewonnene Lösung des Chlorids 0.8*M* war. Diese Grundlösung wurde dann mit der Versuchslösung jeweils auf das Doppelte verdünnt.

Die Bestimmung des Mg^{+2} beruht auf der Tatsache, dass an der strömenden Elektrode kein Maximum auftritt[3], und dass eine solche Elektrode im Gegensatz zu der Tropfenden selbst im negativsten Potentialbereiche verwendet werden

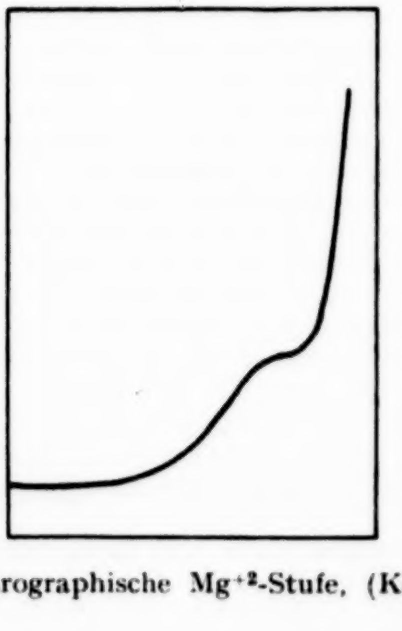

Fig. 2. Die polarographische Mg^{+2}-Stufe, (Konz. = $1 \cdot 10^{-3}$*M*)

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kann. So konnten in 0.4-0.8M $[N(CH_3)_4]$Cl-Leitsalzlösung bei einem pH-Werte von 5.4 bis 6.8 tadellose, gut auswertbare Mg^{+2}-Stufen erhalten werden (Fig. 2). Die Diffusionsströme fanden wir, wie aus der Tabelle I ersichtlich, der Mg^{+2}-Konzentration zwischen $5 \cdot 10^{-4}$ - $3 \cdot 10^{-3} M$ proportional.

TABELLE I

Mg-Ionenkonz. d.Lsg.	*Stufenhöhe*
$5 \cdot 10^{-4} M$	12.0
$1 \cdot 10^{-3} M$	24.0
$2 \cdot 10^{-3} M$	51.0
$3 \cdot 10^{-3} M$	73.5

Die unmittelbare polarographische Bestimmung des Calciums geschieht nun an der strömenden Quecksilberelektrode auch ganz einfach. Als Leitelektrolyt wird hierbei ebenfalls eine 0.4M Lösung von $[N(CH_3)_4]$Cl verwendet, und in einem Konzentrationsbereiche vom $2 \cdot 10^{-4}$ bis $5 \cdot 10^{-3} M$ erhält man einen der Ca^{+2}-Ionenkonzentration stets proportionalen Diffusionsstrom. Die Stufen sind maximumfrei, gut gestaltet, daher einwandfrei auszuwerten (Fig. 3.) und zwischen 4.8 bis 9.4 vom pH unabhängig. Erst unterhalb von pH = 4.5 wird die Auswertung durch die Wasserstoffwelle gestört. In stark alkalischen Lösungen (pH >9.4) werden die Stufen wiederum schlechter definiert und es tritt wahrscheinlich wegen Ausscheidung von $CaCO_3$ ausserdem auch eine Abnahme des Diffusionsstromes auf. Dies ist übrigens nicht von Interesse, da bei der Bestimmung von Ca^{+2} und Mg^{+2} nebeneinander mit Rücksicht auf das Letztere sowieso nur ein etwas sauerer Bereich in Frage kommen kann.

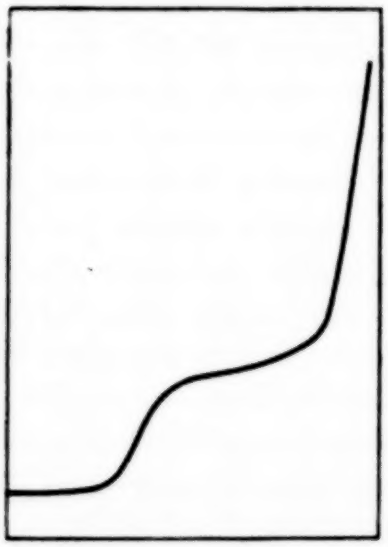

Fig. 3. Die Ca^{+2}-Stufe (Konz. $= 0.8 \cdot 10^{-3} M$)

Die K^+ und Na^+-Ionen geben bei Verwendung der strömenden Quecksilberelektrode, wie stets, nur eine gemeinsame, jedoch ebenfalls tadellose, gut auswertbare Stufe. Die Gestalt der Stufe ist vom pH in weiten Grenzen unabhängig, nur von etwa pH = 4.5 abwärts stört auch hier die Wasserstoffwelle.

Des weiteren haben wir die Polarographie dieser in den Wässern am häufigsten vorkommenden und somit wichtigsten Kationen nebeneinander untersucht. Hierbei spielen natürlich die Halbstufenpotentiale eine ausschlaggebende Rolle; wir haben, um die Fähigkeit unseres neuen Verfahrens mittels der strömenden Elektrode zu zeigen, die ermittelten Potentialwerte tabellarisch zusammengestellt.

TABELLE II

HALBSTUFENPOTENTIALE

Kation	*1*	*2*	*3*
Ka^+	—2.22	—2.15	—2.17
Na^+	—2.23	—2.16	—2.15
Ca^{+2}	—2.46	—2.36	—2.23
Mg^{+2}	—2.64	—2.53	(—2.3)

In der 1. Spalte der Tabelle II sind die Halbstufenpotentiale der genannten Ionen verzeichnet, die an der strömenden Quecksilberelektrode in einer auf Cl^--Ionen $0.4M$ Grundlösung, wie üblich, direkt (mit einer Genauigkeit von ± 20 mV) beobachtet, und nicht mit dem durch den Strom bedingten Spannungsabfall (***i·r***) korrigiert wurden. Bei der Bestimmung der Halbstufenpotentiale wurde, da wir keine besondere Genauigkeit anstrebten, auch keine abgetrennte Gegenelektrode verwendet.

Der Zellenwiderstand betrug 340 **Ω**, da aber durch die $10^{-3}N$ Lösungen ein Strom von etwa 10^{-4} A floss, ergibt sich für die Halbstufenpotentiale eine Korrektion (***i·r***) von einigen Zentivolt. Die dementsprechend korrigierten und gleichzeitig auf die $1.0N$ Kalomelelektrode umgerechneten Werte sind in der Spalte 2. zu sehen. Die 3. Spalte endlich enthält die ebenfalls auf die $1.0N$ Kalomelelektrode bezogenen, jedoch an der tropfenden Elektrode gemessen Halbstufenpotentialwerte[4].

Wie aus der Tabelle ersichtlich, kann eine Trennung der in Frage stehenden Ionenstufen wegen der günstigen Verschiebung der Halbstufenpotentiale eigentlich nur an der strömenden Quecksilberelektrode erzielt werden. Die Halbstufenpotentiale der K^+ und Na^+-Ionen fallen zwar auch hier fast zusammen, so dass diese auch bei unserer Methode nicht separat erscheinen. Die Stufen der Ca^{+2}- und der Mg^{+2}-Ionen aber sind so erheblich verschoben, dass dieselben von einander, sowie

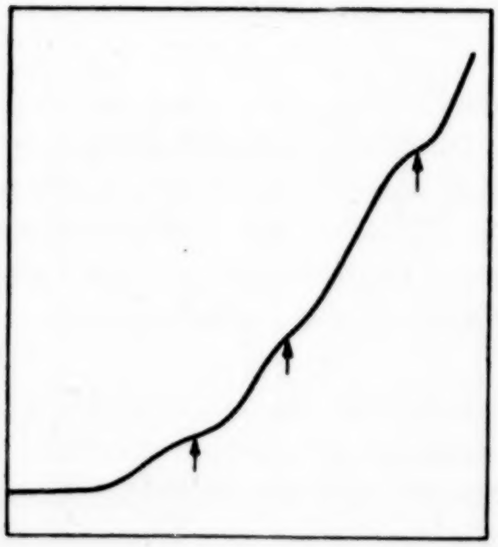

Fig. 4. Das Polarogramm einer Lösung von ($Na^+ + K^+$)-, Ca^{+2}- und Mg^{+2}-Ionen

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von der gemeinsamen ($Na^+ + K^+$)-Stufe leicht getrennt werden können (Fig. 4). Die erwähnte Verschiebung der Halbstufenpotentiale ist in erster Linie natürlich dadurch bedingt, dass die Diffusionsstromstärke bei den angegebenen Versuchsumständen etwa zehnmal grösser als bei derselben Konzentration an der Tropfelektrode, der Widerstand unserer Zelle jedoch von derselben Grössenordnung als der der Tropfzelle war. So stieg das Produkt $i \cdot r$ tatsächlich etwa auf das Zehnfache, und demzufolge verschoben sich auch die beobachteten Halbstufenpotentiale (statt Millivolt) um einige Zentivolt u.zw. nicht einmal äquidistant, weil in der Praxis hier auch das Konzentrationsverhältnis zweier Nachbarionen einen viel stärkeren Einfluss ausübt. Die Werte der Spalten 2 und 3 der Tabelle II lassen sich für die Ca^{+2}- und Mg^{+2}-Ionen (besonders für Letztere) zwar nicht gut vergleichen, doch scheint es, dass für die Verschiebung des Halbstufenpotentials wenigstens im Falle des Ca^{+2}-Ions, ausser den oben erwähnten, auch weitere Faktoren* verantwortlich gemacht werden müssten. Hierauf wollen wir aber diesmal noch nicht näher eingehen.

Unter dem Gesichtspunkte der polarographischen Wasseranalyse ist es interessant, auch die äquivalenten Stufenhöhen der einzelnen in Frage kommenden Ionen (Tabelle III) zu vergleichen.

TABELLE III

ÄQUIVALENTE STUFENHÖHEN

Kation	*h in mm*	$\frac{h}{\sqrt{D}} \cdot 10^3$
Mg^{+2}	23.8	7·10
Ca^{+2}	24.8	7·28
Na^+	25.3	7·20
K^+	26.2	6·54**

** Beim K^+ bedarf dieser Wert immerhin einer Überprüfung.

Hierin sind die Stufenhöhen der Kationen in $2 \cdot 10^{-3} N$ Lösungen verzeichnet, die in der eingangs erwähnten Zelle mit der strömenden Elektrode aufgenommen und als Ordinatendifferenzen der Inflexionspunkte zwischen den Stufen bestimmt wurden. Aus der Tabelle sieht man nun, dass sich die äquivalenten Stufenhöhen, die übrigens auch an der strömenden Elektrode der Quadratwurzel des Diffusionskoeffizienten (D) proportional sind[5], relativ wenig ändern, so dass man z.B. bei Bestimmung der Gesamthärte des Wassers verlässlich auch mit einem Mittelwerte der Äquivalentstufen der Ca^{+2}- und Mg^{+2}-Ionen rechnen kann. Selbst in dem ungünstigsten Falle, d. h. wenn nur das eine der beiden Ionen anwesend wäre, beginge man nur einen Fehler, der nicht über 2% stiege. Dasselbe gilt natürlich auch für die gemeinsame ($Na^+ + K^+$)-Stufe.

Als Beleg für die Brauchbarkeit unserer polarographischen Bestimmungsmethode der Mg^{+2}- und der Ca^{+2}-Ionen (und der Alkalien) nebeneinander, soll die Tabelle IV dienen. Hieraus ersieht man, dass der Fehler sich in mässigen Grenzen hält.

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* Die Diffusionsgeschwindigkeit der Metalle im Hg ist gegen die Erneuerungsgeschwindigkeit der Oberfläche d. h. gegen die Strömungsgeschwindigkeit des Quecksilbers klein. Beim Ca müsste aber etwa eine noch niedrigere Diffusionsgeschwindigkeit angenommen werden, als bei den Alkalimetallen, so dass hier an der Oberfläche ev. eine höhere Amalgamkonzentration herrschen kann.

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TABELLE IV

		Einwage mg	*gefunden* mg	*Fehler* %
1	Ca	0.401	0.419	+4.5
	Mg	0.486	0.470	—3.3
2	Ca	0.802	0.807	+0.6
	Mg	0.486	0.480	—1.2
3	Ca	1.603	1.510	—5.8
	Mg	0.486	0.511	+4.3
4	Na	0.368	0.376	+2.1
	Ca	0.640	0.616	—3.7
	Mg	0.710	0.735	+3.5

Nach diesen Vorarbeiten haben wir die Polarogramme verschiedener natürlicher Wässer aufgenommen und die aus jenen entnommenen Daten in der Tabelle V zusammengestellt, um dieselben mit den mittels der heutzutage als best-angesehenen komplexonometrischen Methode gewonnenen zu vergleichen. Die Daten für die Gesamthärte stimmen recht gut überein. Bemerkenswert ist es aber, dass auch die für die Berechnung von Wasserenthärtungszusätzen so wichtigen Angaben, wie

TABELLE V

Bezeichnung	*Verdünnung*	*Polarographisch*			*Komplexonometrisch*		
		Ca-	*Mg-*	*Gesamt-*	*Ca-*	*Mg-*	*Gesamt-*
		Härte in dtschen Gr.					
Leitungswasser (Budapest)	1:2	9.3	4.1	13.4	9.39	3.68	13.07
Donauwasser (Fig. 5)	1:2	9.5	5.4	14.9	10.10	4.92	15.02
Brunnenwasser I	1:4	25.3	24.0	49.3	25.35	24.20	49.55
Brunnenwasser II	1:4	32.0	22.6	54.6	30.85	23.20	54.05

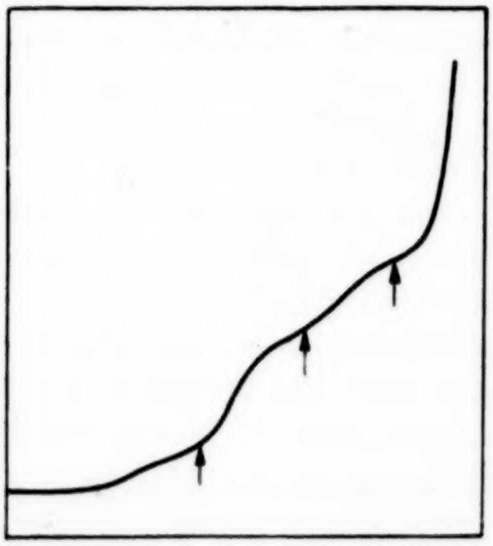

Fig. 5. Polarogramm des Donauwassers (Na^+, Ca^{+2}, Mg^{+2})

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die Konzentrationen der einzelnen Erdalkalimetalle, mit der schnellen polarographischen Methode in fast so guter Übereinstimmung ermittelt werden können. Es soll aber betont werden, dass die komplexonometrische Trennung von Ca und Mg bekanntlich bei Weitem nicht so exakt ist, wie die Bestimmung der Gesamthärte nach demselben Verfahren, so dass Erstere hier eigentlich nicht mehr als Standardmethode herangezogen werden kann.

Wir beabsichtigen demnächst in erster Linie die Genauigkeit der Auswertung unserer Polarogramme durch eine geeignete Derivation zu steigern, sodann aber die polarographische Wasseranalyse auch auf andere Ionen, insbesondere auf die wichtigsten Anionen auszudehnen. Einige unter Letzteren (hauptsächlich SO_4^{-2}) werden natürlich nur polarometrisch zu bestimmen sein, doch verspricht das geschilderte Verfahren in der Wasseranalyse eine grosse Ersparnis an Mühe und Zeit.

ZUSAMMENFASSUNG

Es wurde ein polarographisches Verfahren zur Untersuchung von Trink- und Brauchwasser, insbesondere zur Bestimmung der Härte und der Alkalien ausgearbeitet. Die Arbeit wird zwecks Entwicklung einer vollständigen Wasseranalyse fortgesetzt.

SUMMARY

A polarographic method has been devised for the examination of drinking water and industrial water, and in particular for the estimation of the hardness and the alkalis present. The investigation will be continued with a view to developing a complete analysis of water.

RÉSUMÉ

Une méthode polarographique est décrite pour l'analyse de l'eau potable et de l'eau industrielle, en particulier pour la détermination de la dureté et de la teneur en métaux alcalins. Des recherches sont en cours pour développer une méthode d'analyse de l'eau complète.

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BOOK REVIEW

Practical Organic Chemistry, including Qualitative Organic Analysis by Arthur I. Vogel, Longmans, Green and Co., London, New York, Toronto, 3rd Edition, 1956, XXVII + 1188 pp., 300 illus. £3.

The first and second editions appeared in 1948 and 1951 respectively and received many favourable reviews, including one in this Journal [*Anal. Chim. Acta*, 2 (1948) 286]. For the present edition the entire text has been exhaustively revised and modernised and there is considerable additional matter, leading to an increase in the length of the volume by some 150 pages. An example of up-to-dateness is that mention is made of the carcinogenic properties of β-naphthylamine and the fact that, as a result, this substance is not now manufactured on the commercial scale in Great Britain. For the preparation of β-bromonaphthalene β-naphthylamine is avoided by the use of 2-aminonaphthalene-1-sulphonic acid. A new and valuable feature is the account of the electronic mechanisms (in outline) of the numerous reactions described in the text. Further additions are a chapter on semimicro technique and an appendix describing applications of infrared and ultraviolet spectra to organic chemistry.

After preliminary chapters on theoretical and practical aspects of general technique, the preparation of about 900 compounds is described, by methods which have been tried out by the author and his students, and which incorporate and illustrate the major organic reactions. The book is far from being merely a collection of recipes; it can, indeed, be considered as a general textbook of organic chemistry in which the main emphasis is laid on preparative details.

The chapter on qualitative organic analysis (74 pages) is a comparatively small portion of the book, although it must be borne in mind that in many cases preparation of derivatives (an important part of organic analysis) is given in the main section of the book. The analytical methods described are on a sound basis, emphasis being laid on a study of class reactions and solubility behaviour.

An Appendix gives to the student valuable assistance in searching the literature of organic chemistry.

The book has already made its name and (to quote the original *Analytica Chimica Acta* review) is undoubtedly worth every penny of its moderate cost.

N. Strafford (Manchester)

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